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Equilibrium Arsenic Capacity of Activated Alumina

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16. ABSTRACT

This study of As(V) removal by activated alumina (Alcoa F-1) was designed (1) to determine the As(V) capacity by batch and column methods and to compare the isotherms; (2) to determine the optimum pH for adsorption; and (3) to determine the effect of competition by chloride and sulfate ions.

Batch tests reached an equilibrium solid phase loading of 13.5 mg As(V)/g AA at a liquid phase concentration of 1.0 mg As(V)/L in an water containing 266 mg Cl^-/L and 367 mg SO_4^{2-}/L (pH 6, 25°C). Minicolumn tests under similar conditions obtained a solid phase loading of 16.1 mg As(V)/g AA at 1.0 mg As(V)/L, but yielded results identical to the batch tests at concentrations less than 0.50 mg As(V)/L. These results verified the feasibility of batch tests for modeling column capacities in that range.

Minicolumn tests showed adsorption to be pH dependent: maximum adsorption occurred at pH 6. Increased temperature resulted in increased adsorption, as batch tests at 40°C yielded solid phase loadings 33% higher than at 25°C. The increase was attributed to kinetic rather than energetic considerations. Adsorption from pH 6.0 deionized water reached a maximum loading of 25 mg As(V)/g AA at 1.0 mg As(V)/L and decreased by over 50 percent with 720 mg SO_4^{2-}/L and 16 percent with 532 mg Cl^-/L. These decreases were greater than expected on the basis of previous fluoride experiments.

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THE EQUILIBRIUM ARSENIC CAPACITY OF ACTIVATED ALUMINA

by

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution, and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and is a most vital communications link between the researcher and the user community.

Removal of inorganic contaminants from drinking water supplies presents a considerable challenge to many municipalities throughout the United States. In an effort to assist these communities in the selection of the most effective and economical treatment process, the EPA (in conjunction with the University of Houston) has funded the development of a mobile drinking water treatment pilot plant capable of evaluating four separate pollution removal techniques--reverse osmosis, electrodialysis, ion exchange, and activated alumina. This report presents the results of laboratory research to determine the equilibrium arsenic capacity of activted alumina under conditions similar to those likely to be encountered in the field.

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ABSTRACT

Arsenic(V) can be effectively removed from water by adsorption onto activated alumina. Variables affecting the extent of adsorption include pH, temperature, and the presence of other ions in solution. Adsorption isotherms establishing a relation between solid and liquid phase arsenic concentrations at equilibrium can be developed by batch tests of 7 days or more. Despite the fact that batch tests expose alumina to uncharacteristically high initial arsenic concentrations, the resulting capacities were close to those obtained by minicolumn tests.

Batch tests performed with granular Alcoa F-1 type activated alumina (28 x 48 mesh) required as many as 7 days to reach an equilibrium solid phase loading of 13.5 mg As(V)/g at a liquid phase concentration of 1.0 mg As(V)/L in an artificial groundwater containing 266 mg Cl^-/L and 367 mg SO_4^{2-}/L (pH 6) at 25°C. Minicolumn tests performed under similar conditions obtained a solid phase loading of 16.1 mg As(V)/g alumina at 1.0 mg As(V)/L, but they yielded results identical to the batch tests at equilibrium liquid phase concentrations less than 0.50 mg As(V)/L. These results verified the feasibility of batch tests for modeling column capacities in that range.

Minicolumn tests showed As(V) adsorption to be extremely dependent on pH, as expected, since the latter detemines both the surface charge on the alumina and the valence of the arsenate. Maximum adsorption occurred at pH 6. Increased temperature resulted in increased adsorption, as batch tests performed at 40°C yielded As(V) solid phase loadings 33 percent higher (at 1.0 mg As(V)/L) than tests performed at 25°C. This increased adsorption was attributed to kinetic rather than entropic considerations. As(V) adsorption from deionized water reached a maximum loading of 25 mg As(V)/g alumina at 1.0 mg As(V)/L, which decreased by over 50 percent in the presence of 720 mg SO_4^{2-}/L. These decreases were greater than expected on the basis of previous experiments with fluoride adsorption onto the same type of alumina.

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ABBREVIATIONS AND SYMBOLS

$\mathring{A}$	Angstrom ($1\ \mathring{A} = 10^{-10}$ m)
b	Energy constant in Langmuir adsorption model
BET	Brunauer-Emmett-Teller modification of the Langmuir isotherm used to determine available surface area of adsorbent solids by means of inert gas adsortion
BV	Bed volume; volume occupied by adsorbent in a column, or an equal volume of solution passed through the column
C	Liquid-phase adsorbate concentration
C_e	Liquid-phase adsorbate concentration at equilibrium following adsorption
C_o	Initial or original liquid-phase adsorbate concentration before adsorption
C_s	Liquid-phase adsorbate concentration corresponding to complete saturation of the monolayer; a constant used in the BET adsorption model
EBCT	Empty bed contact time; the time required for a voume of solution equal to the bed volume of adsorbent to pass through a column
FAAS	Flameless atomic absorption spectrophotometry; an analytical method for detecting trace concentrations of arsenic
G	Gibbs free energy; a thermodynamic variable
H	Enthalpy; a thermodynamic variable which includes heat of adsorption
K	Energy constant in Freundlich adsorption model
K_a	Acidity constant, indicating the ratio of deprotonated to protonated species of an ion in solution; also, K_1, K_2 for polyprotic ions
K_a^s	Solid-phase acidity constant, indicating the ratio of deprotonated to protonated species for an ion adsorbed onto the surface of an adsorbent; also K_{a1}^s, K_{a2}^s for polyprotic adsorbed ions
mmol	Millimole; one one-thousandth part of a standard gram mole, or 6.022×10^{20} molecules
meq	Milliequivalent; one one-thousandth part of a standard gram equivalent, or one millimole divided by the molecular valence
n	Energy constant in Freundlich adsorption model

Q	Maximum solid-phase adsorbate concentration; a constant in Langmuir adsorption model
q_e	Solid-phase adsorbate concentration at equilibrium which characterizes an adsorbent by correspondence to an equilibrium liquid-phase concentration
r^2	Statistical deviation of data points from a standard curve
T	Throughput, a measure of adsorption efficiency; the ratio of adsorbate mass passed through a column to the mass of adsorbate retained by the adsorbent (mg/mg)
t_{eq}	Time to equilibrium; for a batch test, time during which the adsorbent and adsorbate are allowed to equilibrate

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SECTION 1

INTRODUCTION

ARSENIC DISTRIBUTION, CHEMISTRY, AND TOXICITY

A significant percentage of all natural surface waters contains trace concentrations (10 ppb) of arsenic [1, 2, 6]. In one recent survey of U.S. surface water [3], 21 percent of the 727 rivers and lakes sampled contains arsenic, and nearly all of those exceeded 10 ppb. Arsenic occurs naturally in certain ground waters, particularly in the southwestern United States (100 to 1400 ppb) [12, 19], Alaska (10,000 ppb) [25], New Zealand [7], and Taiwan (2,000 ppb) [12]. Moreover, industrial and agricultural processes involving arsenic have resulted in toxic effluent concentrations as high as 300 mg/L [18, 13, 5, 11], which in several instances have contaminated local water supplies [3, 6, 8]. According to Ferguson and Gavis, it is probable that arsenic concentrations in natural waters often approach or exceed values thought to be safe for drinking water [1].

Arsenic is stable in four oxidation states (+5, +3, 0, -3) under the redox potential (Eh) conditions occurring in most aquatic systems. Arsenic most commonly appears in solution in the pentavalent (arsenate) form as an anion ($H_2AsO_4^-$, $HAsO_4^{2-}$) of arsenic acid (H_3AsO_4), and in the trivalent (arsenite) form as arsenious acid and its anion (H_3AsO_3, $H_2AsO_3^-$) [1]. The interconvertability of As(III) and As(V) suggests that the arsenate species will predominate in surface waters and other oxidizing conditions, while anaerobic ground waters and reducing conditions will yield arsenic as arsenite. The rate of oxidation of arsenite with oxygen is reported to be very slow at natural pH values [1], although oxidation at moderate pH occurred in this research.

As(III) is generally considered to be at least twice as toxic as As(V) [2, 3, 8]. But according to Harvey [8], regardless of whether an arsenical is introduced into the body as trivalent or pentavalent arsenic, all the major toxic actions can be attributed to the trivalent form, which penetrates the cell membrane more readily than the pentavalent form.

The toxicity of arsenic in humans is principally due to the inhibition of sulfhydryl enzymes by reaction with arsenoxide and arsenite, which is probably the first step in cell damage. While the arsenate ion is capable of uncoupling phosphorylation through the formation of arsenate esters, the significance of this substitution in human metabolism is unknown.

Arsenic affects most major physiological systems. Small doses of inorganic arsenic cause vasodilation, splanchnic hyperemia (resulting in nausea, diarrhea, and vomiting), skin pigmentation, headaches, and anorexia [8]. In

addition, chronic exposure frequently causes the condition of "garlic breath" with excessive salivation and sweating; stomatitis; circumscribed edema; hyperkeratosis, desquamation, and exfoliation; and liver enlargement, jaundice, and renal damage. Chronic exposure may also lead to peripheral arteriosclerosis ("blackfoot disease"), Haff's disease [21], peripheral neuritis, and encephalopathy.

Several cases of chronic arsenic poisoning by contaminated drinking water have been documented. Residents of Antofagasta, Chile, whose water supply for 12 years averaged 800 ppb arsenic, experienced the following clinical symptoms (in order of frequency): abnormal skin pigmentation, chronic coryza, abdominal pain, Raynaud syndrome, chronic cough, acrocyanosis, bronchopulmonar disease, lips herpes, and chronic diarrhea. Children under 10 were most critically affected, and several died from coronary occlusion and thrombosis [9]. Villagers of the southwestern coast of Taiwan whose well water contained up to 2000 ppb arsenic exhibited epidemic incidence of peripheral arteriosclerosis and skin cancer [9]. Arsenical waters in Argentina have been associated with keratosis, hyperpigmentation, and cancers of the skin, respiratory and digestive tracts [3].

Dugan and Lipscombe estimate that dietary intake of arsenic in the United States ranges between 0.136 and 0.330 mg per person per day, and Harvey [8] gives an average intake from all sources (food, water, and air) of 1 mg per person per day. Contaminated drinking water has caused illness at a concentration of 210 ppb arsenic, but others report ingestion of drinking water with up to 250 ppb arsenic without adverse effects [1]. Assuming an upper limit of safety of 0.100 mg per person per day, and drinking water consumption of 2 liters per person per day, the U.S. Environmental Protection Agency (EPA) established a maximum contaminant level (MCL) of arsenic in drinking water of 50 ppb.

ARSENIC REMOVAL FROM WATER SUPPLIES

The presence of measurable levels of arsenic in a significant percentage of surface water sources, and a relatively infrequent occurrence of arsenic in finished water supplies [3] indicates that trace amounts of arsenic are successfully removed by conventional water treatment methods. This inference is supported by experimental data on arsenic removal which has been performed in a number of ways, including coagulation and precipitation, adsorption onto solid media, ion exchange, and reverse osmosis.

Arsenic Removal by Coagulation

Reactions in the environment which tend to remove arsenic from water include adsorption onto clays and coprecipitation with metal ions during coagulation and precipitation [1]. In treatment plants and experimental studies, arsenic has been removed with varying degrees of success by precipitation onto aluminum and iron hydroxides (as well as by lime softening) usually followed by filtration. Of the coagulants, ferric chloride has been most successful. Removal appears dependent upon initial concentration, dosage of precipitate, pH, and the valence of the arsenic species.

Arsenic Removal with Alum

Early alum precipitation experiments by Buswell [10] yielded some removal of high arsenic concentrations (25 mg/L) at pH 6-7. Rosehart and Lee [7] more recently found alum moderately successful in removing high concentrations of arsenic (132 mg/L) from gold mine wastes, affecting a maximum 90 percent removal of As(V) to 13.2 mg/L by addition of alum in an Al/As ratio of 4:1 (alum = 586.7 mg/L) at pH 7-8. Removal of lower concentrations of the trivalent form was also successful: 500 ppb As(III) was reduced 95 percent to 25 ppb under the same optimal dosage and pH conditions.

By comparison, Shen [12] removed only 32 percent of 1000 ppb arsenic with 20 mg/L alum at pH 6.8. The valence was not specified, but this ground water presumably contained As(III).

Gulledge and O'Connor's As^{74} radioiostope experiments on a 50 ppb As(V) tapwater solution reached a maximum removal of 87 percent before filtration with 40 mg/L alum added at an initial pH of 7.0. Filtration of the same test batch yielded a total removal of 91 percent, which was surpassed only by the 92.6 percent removal resulting from a batch precipitated with 50 mg/L alum at pH 6 followed by filtration. Percent As removals obtained at pH 8 were markedly lower, presumably owing to the increasing solubility of aluminum hydroxide above pH 7.

Nillson [14] also investigated alum precipitation of arsenic, removing 94 percent of 21 mg/L As(V) with 100 mg/L alum at pH 6.5-7. However, these same conditions failed to remove any of 23 mg/L As(III). At the same alum concentration, 71 percent and 60 percent removals of 4.2 mg/L As(V) were effected [18].

The most thorough research to date has been performed by Sorg and Logsdon [2] at what was then the EPA Water Supply Research Division treatment plant (Cincinnati, Ohio). They achieved a maximum removal, before filtration, of 74 percent of 160 ppb As(V) with 25 mg/L alum at pH 7.3, reaching 95 percent removal after filtration with anthracite and sand; 96 percent with alum plus exhausted GAC filtration; and 94 percent with alum plus virgin GAC filtration. By contrast, only 14 percent of 160 ppb As(III) was removed by 29 mg/L alum at pH 7 before filtration, while subsequent filtration with dual media removed a total of 21 percent As(III); exhausted GAC, 35 percent; and virgin GAC, 44 percent.

Arsenic Removal with Iron Coagulation

Similar precipitations with some form of iron have been performed (often in conjunction with alum precipitation experiments) principally with either ferric or ferrous sulfate, or ferric chloride.

With subsequent filtration, Buswell [10] removed 84 percent of 25 mg/L As(V) by adding about 250 mg/L of "Ferrisul" ferric sulfate at pH 5-6, and achieved similar removal (to 4 mg/L) of As(III) after it was oxidized to As(V) with calcium hypochlorite.

Cherkinskii [15] reported 96 percent removal of 362 mg/L arsenous oxide with ferrous sulfate added at 750 mg/L.

Rosehart and Lee [17] also removed 94 percent of 132 mg/L As(V) with ferrous sulfate in an Fe/As ratio of 1.5 at pH 8, but failed to remove any of the 500 ppb As(III) by this method. However, ferric chloride added at an Fe/As ratio of 4.0 removed 90 percent of 132 mg/L As(V) and 95 percent of 500 ppb As(III) at pH 9 and pH 8, respectively.

With ferric sulfate doses of 30 mg/L and higher, Gulledge and O'Connor [13] demonstrated nearly complete removal of 50 ppb As(V) over a pH range from 5 to 8. Maximum removal before filtration (96.5 percent) occurred with 50 mg/L added at pH 7.5 resulting in a post-filtration removal of 97.5 percent, to 1.25 ppb. The highest overall removal (99.9 percent) was achieved with addition of 40 mg/L ferric sulfate at pH 7.5.

After testing both ferrous sulfate and ferric chloride, Shen [12] chose the latter for his treatment plant; 20 mg/L ferrous sulfate added at pH 6.87 removed only 24 percent of 1000 ppb arsenic (probably As(III)), while ferric chloride removed 82 percent, reducing the As concentration to 180 ppb. As expected for the arsenite species, removal was dramatically improved when the solution was oxidized prior to precipitation: prior addition of 20 mg/L chlorine boosted removal to 98.7 percent of the 800 ppb arsenic originally present.

Sorg and Logsdon [2] achieved 81 percent removal before filtration of 390 ppb As(V) by adding 25 mg/L ferric sulfate at pH 6.7 in their pilot plant. After coagulation and dual media filtration, arsenic removal reached 96 percent; after coagulation and GAC filtration, 98 percent removal was obtained. Equally high removal rates were achieved with 30 mg/L ferric sulfate added to 260 ppb As(V) at pH 8. Good results were also obtained for removing As(III) with ferric sulfate, but only at very low arsenic concentrations. By comparison, 30 mg/L ferrous sulfate added at pH 8.6 removed 62 percent of 810 ppb As(V). After coagulation and filtration, removals were 70 and 73 percent, respectively. These results correspond well with the Sorg and Logsdon [2] jar tests, which demonstrated that, for a given dosage of coagulant, percent removal will decrease with increasing initial arsenic concentration above an optimal level.

Pierce and Moore [16] obtained very high removal rates with amorphous $Fe(OH)_3$, up to 119 mg/g at 0.53 mg As(V)/L and 37.5 mg at 0.83 mg As(III)/L.

Arsenic Removal by Lime Softening

Lime softening, as generally practiced, effectively removes arsenic apparently through coprecipitation of arsenic on the hydrous magnesium oxide floc.

In the previously cited Cherkinskii investigation [15], the same percent removal of arsenious oxide (96 percent, from 362 mg/L to 15 mg/L) was accomplished with 2250 mg/L of calcium oxide--three times the concentration needed for ferrous sulfate-induced arsenic removal. Nevertheless, Cherkinskii preferred lime because of its relatively small precipitated volume. Lime was also used to simultaneously soften and remove arsenic from waters in Argentina, sometimes in conjunction with ferric sulfate, and followed by filtration. Hard, turbid waters were treated with lime alone, and recarbonated to

adjust pH [13]. Unfortunately, neither the magnesium concentration nor the pH was given in these references.

Nillson [14] pretreated tap water with phosphate (6 mg P/L) before attempting precipitation with lime, but without success. At pH 9.5, none of the 25 mg/L As(III) was removed. However, when he performed the same experiment on settled ("mechanically treated") municipal wastewater, he observed a 30 percent reduction of As(III), to 16 mg/L. When lower concentrations of As(V) were treated with lime to pH 9.5, as much as 98 percent removal was effected--from 4.2 to .1 mg/L. Again, the magnesium concentrations of the waters were not cited.

Rosehart and Lee [11] found lime effective in removing 95 percent of soluble arsenic of both species. When streams with 132 mg/L As(V) and 500 ppb As(III) were raised to pH 12 with CaO, their arsenic contents were reduced to 6.6 mg/L and 25 ppb, respectively. The optimal Ca/As ratio was 9.8. They also found NaOH pH adjustment to pH 10 an appropriate method for removing arsenic from mining waste streams replete with other heavy metals, viz., iron, copper, and zinc. By adjusting the pH of one such stream to 10, they removed 80 percent of 132 mg/L As(V); apparently, the arsenic coprecipitated with the iron and zinc hydroxides.

In his summary of treatment technologies, Patterson [18] reports 85 percent removal of 0.2 mg/L arsenic to 30 ppb through lime-water softening. Shen [12] observed 20 percent removal when 1000 ppb arsenic was dosed with 20 mg/L lime at an initial pH of 6.9, but he did not record the final pH attained.

Sorg and Logsdon [2] report adequate removal efficiencies in the WSRD pilot plant when final pH after lime addition reached 10 and above. The 400 ppb As(V) samples were within the 50 ppb MCL at removal levels of 89 percent and above; at pH 10.5, removal reached almost 100 percent. As(III), on the other hand, was only 80 percent removed at pH 11.1. Other tests at the pilot plant demonstrated much improved removal at pH 11.3 over pH 9.5--99 percent removal of 580 ppb As(V) after lime softening and filtration versus 53 percent removal of 520 ppb As(V); and 72 percent removal of 340 ppb As(III) versus 26 percent removals of arsenic with lime decreased past a certain optimal initial concentration level. They concluded that if the initial As(III) levels are less than 100 ppb, preoxidation is not necessary to achieve reduction to the MCL when softening is done at pH 10.6 or above; while in the same pH range, samples of up to 350 ppb As(V) could be successfully treated to less than the MCL.

Arsenic Removal by Filtration

A good amount of specific filtration data has accumulated as a result of pilot and full scale experiments with arsenic coprecipitation and subsequent filtration. For example, in designing his full-scale well-water arsenic removal facility, Shen [12] determined that dual media (anthracite and sand) filtration alone was effective in removing arsenic from 850 ppb to less than 10 ppb--when the length of the filtration tube reached 70 cm. In general, he found slow (1-5 m/day) more effective than fast sand filtration (100-200 m/day), but the usable time between regenerations was too short to be practical; only five days.

Sorg and Logsdon [2] found that subsequent filtration could remove up to 80 percent of the remaining arsenic, when the original coagulation lowered the level below 100 ppb. However, they ascribed any differences between dual media and GAC filtration to removal of particulate turbidity rather than adsorption of dissolved arsenic.

Arsenic Removal by Adsorption onto Alumina

Bellack [7] removed arsenic from ground water with activated alumina (F-1 grade Alcoa, 28-48 mesh) in 18.5 mm dia. columns to a height of 25 cm at an optimum flow rate of 2 1/2 to 3 gpm/ft^2. Breakthrough appears to have first occurred after 417 bed volumes of 1 mg/L arsenic had been treated. Regeneration with four bed volumes of caustic eventually raised the cycle length of 1044 bed volumes, and during treatment the pH of the water was reduced from 9.3 to 7.1.

Gupta and Chen [20] investigated adsorption of arsenic by activated alumina, activated bauxite, and activated carbon. The equilibrium isotherms they developed suggested that arsenic (V and III) was most strongly adsorbed onto activated alumina.

Although their reasoning is hard to follow because of the manner in which they performed their experiments and presented their data (e.g., initial rather than final As concentrations were reported), their qualitative conlcusions can generally be substantiated by careful scrutiny and interpretation of their data. Regarding the adsorption of As(V) on alumina, they found that the equilibrium adsorption capacity of alumina was approximately constant at 7.5 mg As(V)/g alumina when the final As(V) concentration was 300 ppb. Furthermore, they indicated that adsorption at that concentration was not much affected by the salinity of the solution. (These values were not stated, but had to be calculated from the extrapolated linearized Langmuir isotherms.) However, when the equilibrium As(V) concentration was 50 ppb, the final capacity of the adsorbent varied from 1.0 mg As(V)/g alumina for sea water to 4.2 mg As(V)/g alumina for fresh water (analysis not given). No explanation for the observation that increasing salinity decreased arsenic adsorption was proposed. It can be presumed, however, that the primary effects were simply due to chloride and sulfate ion competition since they probably varied drastically. They also observed that increasing the salinity decreased the rate of adsorption, e.g., it took about one hour to attain 80 percent of equilibrium and 24 hours to achieve 95 percent of equilibrium for arsenic adsorption from an agitated fresh water and about twice that long for sea water. Not unexpectedly, they found that the As(V) capacity of the alumina was very much a function of pH; it decreased markedly at pH above 7, probably due to hydroxide competition rather than the conversion from the monovalent to the divalent arsenate ion as proposed.

Although one would expect the adsorption of As(III) on alumina to be pH dependent in the 4 to 9 range, such was not the case in Gupta and Chen's experiments. Between pH 4 and the optimum pH of 9, they found that a nearly constant amount of As(III) (9.0 mg/mg) was adsorbed on the alumina in equilibrium with As-containing fresh waters. Since the pK_1 for arsenious acid is 9.22, the predominant form in the 4 - 9 range is the neutral $HAsO_2$ ($As(OH)_3$ or H_3AsO_3) species and its pick-up by alumina would be expected to be negligible

if ion exchange is the only mechanism involved. This phenomenon should be further investigated as all means of removing As(III) including precipitation, adsorption, and membrane rejection have been reported to do a poor job in removing the reduced form of arsenic, because it (arsenite) is not an ion at neutral to low pH.

Competitive adsorption experiments with silica indicated significant competition at silica concentrations of 70 mg/L and higher when As(V) concentrations were around 4 mg/L, and As(III) concentrations were around 1 mg/L. This is in accord with what would be expected since silica, especially the ionic form, is a highly preferred ion by alumina [21].

Studies of GAC adsorption supported the conclusion of Sorg and Logsdon [2] that GAC is not a particularly good adsorbent of arsenic [20].

Arsenic Removal by Ion Exchange

Because of the inherent advantages of packed beds over simple precipitation and filtration removal methods for treating ground waters, adsorption by a variety of sorbents has been and continues to be investigated.

Calmon [22] tested anion and cation exchangers on "field waters" containing 68 mg/L arsenic. Cation exchangers were ineffective, but batch-type equilibrium tests with several different anion resins in the chloride form showed removals of 55-82 percent. Column tests yielded removals of 99 percent and 100 percent when the column was regenerated with NaOH and HCl, respectively, although in neither case was recovery of adsorbed arsenic complete. No relevant time or other rate information was available.

Shen [9] also ran column tests with the Ionac A-260 weak base resin, but after only 26 bed volumes of synthetic water containing 1 mg/L As(III) had passed through his 2.2 x 60 cm column, only 21 percent of the arsenic had been removed. Lack of pH data renders these results confusing and general success of the same process with subsequent tests made on actual As-containing ground waters emphasizes the fact that some important experimental conditions, viz., pH and buffer capacity, were not measured.

Lee and Rosehart [23] also performed several tests of various ion-exchange resins with limited success. The strong-base resin--Amberlite IRA 400--was reported to adsorb 10^4 mg arsenic/gram resin per mg arsenic/mL solution at pH greater than 3. This ratio reduces to a loading of 10 mg/g for arsenic concentrations encountered in mining wastes. A weak base resin (Amberlite IR-45) demonstrated a loading capacity of 1 mg/g per ppm arsenic at pH less than 2, and the intermediate base resins (Dowex FPS 4015 L and Dowex FPS 404 L) were somewhat less effective (at pH 5-8 and less than 2, respectively). All resins were easily regenerated up to 90 percent recovery of adsorbed As with NaCl; elution was assumed to conform to a square-wave pattern. Effluent concentration histories, on the other hand, increased gradually, with breakthrough presumably As(III) occurring after 170 and 611 bed volumes of solute had passed through the weak (pH 2.3) and strong (pH 9.2) columns, respectively. Columns were 1 cm in diameter, and bed depth was 708 cm. Activated carbon showed poor As adsorption and its study was discontinued.

Single-bed ion exchange with chloride-form strong base anion (SBA) resin is probably capable of complete (> 97 percent) As(V) removal; however, as mentioned in the literature, low resin capacity is a problem. This is understandable in light of the probable position of arsenate in the known selectivity sequence of common ions in SBA exchangers:

$$\text{known:} \quad SO_4^{2-} > HPO_4^{2-} > NO_3^- > Cl^- > HCO_3^- > H_2PO_4^-$$

$$\text{estimated:} \quad SO_4^{2-} > HAsO_4^{2-} > NO_3^- > Cl^- > HCO_3^- > H_2AsO_4^-$$

The divalent $HAsO_4^{2-}$ which is analogous to HPO_4^{2-} is expected to be less preferred than sulfate while the monovalent $H_2AsO_4^-$ analogous to $H_2PO_4^-$ is expected to be even less preferred than bicarbonate. Thus, in the usual ground water situation, with competition from much higher concentrations of SO_4^{2-}, Cl^-, and NO_3^-, the amount of As(V) on the column should be quite small relative to these other ions at the first arsenic breakthrough, $H_2AsO_4^-$. However, anion exchange with a chloride-form strong base resin might be a preferred arsenic removal method for low TDS waters (< 300 ppm), especially if SO_4^- is low.

Arsenic(V) capacity of weak base resins is expected to be even less than that for strong base resins. As discussed in the literature survey, Lee and Rosehart [23] found this to be true. The reason is that weak base resins have ion exchange capacity only at low pHs. Based on the titration curves of Clifford [24], the weak base resin, IR 45, used by Lee achieves its advertised capacity (~ 1.8 meq/mL) only at pH < 2.5. In that pH range, the least preferred $H_2AsO_4^-$ and the non-preferred H_3AsO_4 forms predominate.

In summary, strong base anion (SBA) exchange at neutral pH is probably a poor choice for As(V) removal because of the relatively low preference SBA resins have for the predominant forms of arsenic existing in the neutral pH range. Weak base anion exchange at low pH (2.5) is an even poorer alternative for the same reason. Limited testing with both strong and weak base resins must be done to verify these conclusions on a pilot scale.

Arsenic(III) removal by chloride-form strong-base ion exchange is much more difficult than As(V) removal, since As(III) exists predominantly in the non-ionized form, H_3AsO_3 ($HAsO_2 \cdot H_2O$), at pH less than 9.22, i.e., the pK_1 of H_3AsO_3. The column will not take up appreciable amounts of H_3AsO_3 and the present As(III) removal cannot be greater than the percent anion ($H_2AsO_3^-$) present. This suggests that below pH = 9, less than half the As(III) will be removed in strong base anion exchange; that trend has been observed in the results of Sorg and Logsdon [2]. Only a limited amount of testing with strong base resins in the chloride form should be done for As(III) removal unless the results of those tests indicate that these predictions are in error.

There would appear to be no real hope of applying weak base resins to As(III) removal since, at the low pH at which they must operate, As(III) exists almost completely (> 99.9 percent) as nonionic H_3AsO_3 which would only be removed during the very early portions of a two-bed run. At that time, the effluent pH would be above 9.0 due to neutralization of the acid from the first bed by the base form of the weak-base anion exchanger.

Arsenic Removal by Reverse Osmosis

Preliminary studies by Fox [25] show reverse osmosis effective in removing arsenic of both species from water. Below 750 ppb, As(V) is reduced below the minimum detectable resolution by both the DuPont (Aramid) and the Osmonics (cellulose acetate) membranes. The DuPont membrane reduces As(V) below the MCL (50 ppb) when initial concentration is less than 4 mg/L; the Osmonics, when As(V) is less than 6 mg/L. Maximum As(III) removal for either type was 80 percent in this pilot plant. In addition to arsenic, over 90 percent of all hardness was removed by the membranes at pH less than 7 [8].

SECTION 2

THEORY

ACTIVATED ALUMINA

Activated alumina is the common name for aluminum oxide (Al_2O_3), a white crystalline compound normally prepared by thermal dehydration of an aluminum hydroxide (gibbsite, bayerite, etc.). "Activity" here refers to the capacity of alumina to enter into adsorptive and/or catalytic reactions, and is determined largely by such variables as crystal structure, pore size distribution, and the chemical nature of the surface [26, 27]. Activated alumina has been used in packed bed processes for the past 30 years for the removal of inorganic contaminants (especially fluoride) from drinking water [21]. More recently, researchers have investigated the structural characteristics and surface chemistry of activated alumina and their relation to the mechanisms of adsorption.

Structural Characteristics

Several forms of activated alumina have been classified according to the temperatures at which they were obtained from the hydroxide form. The form of alumina most frequently employed as an adsorbent and the one used in this study is the γ-group (γ-Al_2O_3), a low-temperature alumina obtained by dehydration at temperatures less than 600°C. One possible dehydration sequence for the preparation of γ-alumina is represented by Lippens and Steggerda [27] as follows:

$$Al(OH)_3 \text{ (gibbsite, bayerite)} \xrightarrow{180^\circ} \text{boehmite} \xrightarrow{450^\circ} \gamma\text{-}Al_2O_3$$

This class of alumina is further characterized by a crystal structure described as "defect spinel," a cubic, close-packed lattice with two and two-thirds vacancies on the octahedral positions of the unit cell. the occurrence of sharp and diffuse lines in the diffraction patterns of γ-alumina indicates that the lattices are strongly disordered [27].

The pore structure of γ-alumina consists of both macro- and micropores. Decomposition of gibbsite and bayerite at relatively low temperatures yields BET surface areas of up to 500 m^2/g, of which only a small part is present in pores wider than 20 Å [27]. The presence of an extensive micropore system is also substantiated by recent acid/base regeneration studies. Clifford and Chou [28] determined that the BET area of alumina significantly decreased after 108 acid/base regeneration cycles, while the total volume occupied by

the alumina remained almost unchanged. Surface area and other characteristics of the alumina used in this study are presented in Table 1.

Surface Chemistry

Because the metal ions in the surface layer of γ-aluminum oxide have a reduced coordination number, they behave as Lewis acids (i.e., electron acceptors). Schindler [29] has proposed a sequence where, in the presence of water, metal oxides become hydroxylated by (1) coordination, and (2) dissociative adsorption of water molecules. While hydroxylation rates and concentrations differ among metal oxides, hydroxyl groups reportedly form rapidly on the surface of γ-alumina. Gravimetric studies by Peri indicate a concentration of one hydroxyl site per 2.7 $Å^2$ of surface area [27].

Further infrared spectroscopic examination offers evidence for the presence of five different types of hydroxyl ion sites on the surfaces of γ-alumina, corresponding to the number of oxide molecules associated with each hydroxyl group [27, 29]. These sites have been described as increasing in both acidity and chemical activity as the number of oxide neighbors is increased from zero to four. Nevertheless, some researchers maintain that apparent homogeneity is characteristic of certain adsorption reactions, and many current adsorption models of considerable practical value assume all site energies to be equal.

ADSORPTION ONTO ACTIVATED ALUMINA

Like all physicochemical processes, adsorption of a solute onto a solid-solution interface can be described in terms of the thermodynamic relations of reactants and products. At this juncture in the development of adsorption theory, the two main areas of investigation are the nature of the forces of adsorption and the location of their action.

Free Energy of Adsorption

Forces involved in adsorption of an ion onto a metal oxide surface (such as activated alumina) include surface tension and solvation, chemical bonding, and electrostatic attraction. These forces have been related to the overall free energy of adsorption as follows:

$$\Delta G_{ads} = \Delta G_{coul} + \Delta G_{solv} + \Delta G_{chem}$$

signifying the Gibbs free energies of adsorption, electrostatic attraction, solvation, and chemical bonding, respectively [30]. Solvation energy, in this case, refers to the energy involved in hydration of an ion, which becomes available when the ion is adsorbed and is separated from the solvent water molecules. As anions are considered to be less hydrated than cations, and the effect of other forces are more immediately apparent, most investigators have preferred to emphasize the interplay of chemical and electrostatic forces, such that the above equation can be rewritten:

TABLE 1. Characteristics of Alcoa F-1 Type Activated Alumina [28]

	New	Regenerated[1]
Surface Area (BET)	253 m^2/g	208 m^2/g
Mesh Size	28 x 48	28 x 48
Average Pore Radius	16 Å	36 Å
% Surface Area[2] in Pores of Radius		
0 - 15 Å	65.8	19.8
15 - 30 Å	29.8	48.4
30 - 50 Å	1.9	21.2
50 - 100 Å	1.2	8.0
> 100 Å	1.4	2.6

[1]Regenerated alumina subjected to 108 acid/base cycles consisting of 30 minutes 0.5 N H_2SO_4 and 60 minutes 0.25 N NaOH per cycle.

[2]Surface areas were measured by a Micromeritics Model 2500 Digisorb surface area analyzer

$$\Delta G_{ads} = \Delta G_{chem} + zF\psi_s$$

where z is the valence of the adsorbate, F is Faraday's constant, and ψ_s is the potential between the adsorbate and the surface of the adsorbent [30].

According to Hingston [30], the chemical component of the free energy of adsorption is constant and accounts for the specific adsorption of some ionic species, regardless of the sign of the surface charge. The term "specific adsorption" is used for all adsorption that cannot be accounted for solely by electrostatic forces; the forces of specific adsorption are generally classified as London or van der Waals forces, and may reach values of up to -24 kJ/mol [30].

The electrostatic state of a surface depend on the spatial distribution of free (electronic or ionic) charges in its neighborhood [26]. Beginning with the work of Stern [31], this distribution has been idealized as an electrical "double layer": a fixed charge or surface charge attached to the solid surface resulting in a plane of high potential (compact, or Stern layer), followed by a region of lesser charge determined by the adsorbed ions with a lower potential distributed diffusely into the bulk solution (Guoy layer). Subsequent workers have further divided these theoretical layers. For instance, Davis (after Bowden *et al.*) [29] splits the Stern layer into an inner and outer layer, while between the Stern and Guoy layer, Tezak [26, 29] postulates alternating layers of counterions and coions. In most cases, hydroxylation of the metal oxide surface is considered to occur in the region of compact charge, while the resultant change in potential is thought to affect the extent of further adsorption.

Surface Charge

As mentioned above, the surface of activated alumina readily hydroxylates in water. Further hydrolysis results in the ionization of functional groups, the degree of which is dependent upon the pH of the solution. The sequence of these reactions can be described as follows [29]:

$$\overline{AlOH_2^+} \xrightarrow{K^s_{a1}} \overline{AlOH} \xrightarrow{K^s_{a2}} \overline{AlO^-}$$

where $\overline{AlOH_2^+}$, $\overline{AlOH^-}$, etc. represent solid phase concentrations of hydronium and hydroxide ions. The acidity constants K^s_{a1} and K^s_{a2} incorporate both dissociation of the proton from the surface group in a hypothetically chargeless surrounding and its subsequent removal into the bulk of the solution. The last is accounted for by a Boltzmann distribution factor which represents the coulombic energy of interaction. Thus,

$$K^s_{a1} = \frac{[H^+]\ \overline{AlOH}}{\overline{AlOH_2^+}} \exp(-F\psi^s_{H^+}/RT)$$

and

$$K^s_{a2} = \frac{[H^+]\ \overline{AlO^-}}{\overline{AlOH}} \exp(-F\psi^s_{H^+}/RT)$$

where $\psi^s_{H^+}$ is the effective electric potential at the locus of adsortpion compared to a bulk potential of zero [31].

While the ratio of different charged groups on the surface can only be measured in an ionic medium of some kind, the values of the surface acidity constants have been extrapolated to the theoretically chargeless situation. For example, Stumm and Huang [29] have reported values of K^s_{a1} and K^s_{a2} for γ-alumina in 0.1 N $NaNO_3$ of 6.51 and 8.43, respectively.

A useful concept with respect to the understanding of adsorption onto metal oxide surfaces is the zero point of charge, defined as the proton condition in which the surface is uncharged by functional groups, i.e., when $\overline{AlOH_2^+} = \overline{AlO^-}$ [26]. In the absence of specifically adsorbed ions (other than H^+ or OH^-), this situation also corresponds to the isoelectric point, the pH at which the solid particle itself is electrokinetically neutral. In that case,

$$pH_{zpc} = pH_{iep} = 1/2\ (pK^s_{a1} + pK^s_{a2})$$

When specifically adsorbed ions are present, however, the pH_{zpc} no longer equals the pH_{iep}, since the additional surface charge changes the pH at which the particle is electrokinetically neutral [26, 29]. For example, anionic adsorption results in a surface with a higher negative charge, hence a larger concentration of hydrogen ions in the bulk solution is required to neutralize the surface, and the pH_{iep} drops. On the other hand, the lower pH_{iep} results in an increase in surface protons, so the pH_{zpc} increases. The pH_{zpc} varies with the treatment history of alumina, but a range of values has been obtained by various researchers. Stumm and Morgan [26] report a pH_{zpc} for -AlOOH of 8.2, while Choi [44] observed an increase in pH_{zpc} from 7.3 to 8.9 as acid-washed alumina was aged in deionized water.

The Role of pH in Adsorption

The relation between pH and adsorption onto alumina has been idealized in terms of an adsorption "envelope" [26, 29, 30] containing the pH interval throughout which adsorption occurs. Just as the charge on the surface of the adsorbent varies with pH, so the adsorbate itself may become more or less ionic, depending upon the acidity of the bulk solution. The adsorption envelope is therefore divided into ranges of increasing and decreasing adsorption, determined by the electrochemical condition of both adsorbent and adsorbate.

For example, the pH-dependence of anonic adsorption onto alumina can be understood as a result of the following two-step process:

1) First, increasing pH results in an increased proportion of adsorbate in the anionic form, increased potential between the alumina and the adsorbate in solution, and hence increased adsorption.

2) As pH increases past its pK_a, the adsorbate is deprotonated further until it is almost entirely present in the anionic form. From that point on, increase in pH yields an increasing proportion of hydroxyl ions in the liquid phase which compete with the adsorbate for surface sites and reduce potential between adsorbent and adsorbate in solution by promoting deprotonation of positively charged sites, all of which results in decreased adsorption.

Bowden et al. [33] developed a model to quantify the effect of pH upon adsorption by means of charge density equations. As mentioned earlier, they split the electric double layer into three parts comprising (1) an inner compact layer of highly structured charges effectively within the solid; (2) a layer of specifically adsorbed ions adjacent to the surface at a finite distance from the first plane; and (3) a diffuse layer extending into the bulk solution.

The charge density of the first layer (σ_s) is defined by binding constants similar to the intrinsic adsorption constants (K_a^s) proposed by Schindler, while the charge density of the diffuse layer (σ_d) is determined according to the Guoy-Chapman theory as a function of the plane potential of the outer compact layer. The charge density of the layer in which specific adsorption of ions occurs is determined by the equation:

$$\sigma_i = \frac{Q_2 z_i K_i X_i \exp(-z_i F \psi_d / RT)}{1 + K_i X_i (\exp(-z_i F \psi_d / RT)}$$

where

Q_2 = maximum possible adsorption in the second layer (eq/cm^2)
z_i = valence (including sign) of ionic species i
K_i = binding constant of ionic species i
X_i = mole fraction of ionic species i
ψ_d = surface potential of the outer compact layer

Charge densities of the three layer are related by the electrical neutrality of the surface, such that $\sigma_s + \sigma_i + \sigma_d = 0$. Thus, adsorption can be related to pH through the σ_i term, which increases as pH increases until X_i reaches its maximum; past that point (around the pK_a of the ionic species), adsorption decreases with pH, as reflected in the continuously decreasing coulombic term $\exp(-zF\psi_d/RT)$, which represents decreasing potential with increasing pH.

General Adsorption Models

Several other mathematical models have been proposed to quantify the forces at work in the adsorption reaction. Among the earliest is the Langmuir model which describes monolayer adsorption onto surface sites of equal energy [34]. The Langmuir equation relates solid phase loading (q_e) to liquid phase concentration at equilibrium (C_e) as follows:

$$q_e = \frac{Q\ b\ C_e}{1 + bC_e}$$

where Q represents the maximum solid phase loading and b is an energy constant related to heat of adsorption. Langmuir constants are obtained from empirical data by plotting the linearized equation

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{Qb}\frac{1}{C_e}$$

where $1/Q$ is the intercept and b is derived from the inverse of the slope of the plot of $1/q_e$ versus $1/C_e$.

The Freundlich model describes adsorption in terms of adsorbate concentration according to the equation $q_e = kC_e^{1/n}$. It allows for adsorption onto sites of unequal energy, where, for instance, the Langmuir constant b varies with the extent of adsorption [34]. Constants are derived from empirical data by analysis of the linearized equation $\log q_e = \log K + (1/n) \log C_e$, where $\log K$ is the intercept and $1/n$ the slope of the $\log q_e$ versus $\log C_e$ plot.

A later modification of the Langmuir isotherm model also assumes homogeneous site energies, but allows for multilayer adsorption. The BET model includes a C_s term designating the liquid phase adsorbate concentration at which the solid surface becomes saturated and multilayer adsorption ensues, such that

$$q_e = \frac{Q\ b\ C_e}{(C_s - C_e)\ [1 + (b - 1)\ (C_e/C_s)]}$$

These constants can also be derived from a slightly more complicated linearized equation

$$\frac{C_e}{(C_s - C_e)q_e} = \frac{1}{bQ} + \frac{(b - 1)C_e}{(bQ)\ C_s}$$

$1/bQ$ is the intercept and $(b - 1)/bQ$ the slope when $C_e q_e$ is plotted against C_e/C_s.

All of these models have found wide acceptance for use in describing adsorption reactions. However, their ability to predict the extent of adsorption reactions under varying conditions is limited by the energy constants involved, which change with such variables as temperature and pH. The model by Bowden *et al.* [33] presented above was specifically developed to provide intrinsic adsorption terms constant over a range of pH values, but its complexity precludes its use in most design situations.

Adsorption in the Presence of Competing Ions

Alumina has been characterized as an amphoteric ion exchanger, capable of both anionic and cationic exchange by virtue of the oppositely charged functional groups (H^+, OH^-) which can be specifically adsorbed onto its surface [35]. Since in both cases, the hydronium and hydroxide ions are highly preferred species, alumina can be considered as either a weak acid cation exchanger or a weak base anion exchanger. Clifford et al. [21] have proposed a simplified picture of fluoride adsorption onto alumina as an anion exchange reaction, involving the following three-step process of acidification, ion exchange, and regeneration:

1) Acidification

$$\text{Alumina-HOH} + \text{HCl} \longrightarrow \text{Alumina-HCl} + \text{HOH}$$

2) Ion Exchange

$$\text{Alumina-HCl} + \text{NaF} \longrightarrow \text{Alumina-HF} + \text{NaCl}$$

3) Regeneration

$$\text{Alumina-HF} + 2\text{NaOH} \longrightarrow \text{Alumina-NaOH} + \text{NaF} + H_2O$$

At this point, repeating the original acidification step yields

$$\text{Alumina-NaOH} + 2\text{HCl} \longrightarrow \text{Alumina-HCl} + \text{NaOH} + H_2O$$

and the ion exchange process may be resumed.

As in the other ion exchange reactions involving multicomponent systems, coions in the adsorbate solution are thought to compete for available adsorption sites on the alumina surface. Clifford et al. [21] have proposed an ion selectivity sequence for anion adsorption as follows (after Umland):

$$OH^- > PO_4^{3-} > F^- > SO_4^{2-}; [Fe(CN)_6]^{4-}; CrO_4^{2-} > [Fe(CN)_6]^{3-};$$

$$Cr_2O_7^{2-} > NO_2^- > Br^- > Cl^- > NO_3^- > MnO_4^- > ClO_4^- > CH_3COO^-$$

When an ion does not match any in the above sequence, or when the selectivity for a series has not yet been determined, Hingston [30] has suggested an equation to relate solid phase equilibrium concentrations of competing anions by means of their Langmuir coefficients. For example, to determine the relative selectivity of alumina for phosphate and selenium,

$$\frac{\overline{P}}{\overline{Se}} = \frac{b_P\ [P]}{b_{Se}\ [Se]}$$

where [P] and [Se] are the liquid phase adsorbate concentrations, P and Se are the solid phase concentrations, and b_P and b_{Se} the Langmuir constants for the individual adsorption of the two ions.

SECTION 3

EXPERIMENTS

OBJECTIVES

Experiments were designed to accomplish the following objectives:

1) to establish the conditions necessary to generate an equilibrium isotherm for adsorption of arsenic(V) onto activated alumina by the batch method;

2) to compare the equilibrium isotherm obtained by the batch method with that obtained from minicolumn operation;

3) to determine the optimum pH for adsorption of arsenic(V) onto activated alumina;

4) to determine the effect of temperature on adsorption of arsenic(V) onto activated alumina; and

5) to determine the effect of competition by chloride and sulfate ions upon adsorption of arsenic(V) onto activated alumina.

Batch and column tests were also conducted to establish isotherms and optimum pH for adsorption of arsenic(III), but without success. Failure was due to premature oxidation of arsenic(III) to arsenic(V), which invalidated the reuslts. A report of these tests is included in the appendix, along with a description of the analytical method developed to distinguish between arsenic(III) and arsenic(V).

REAGENTS

All arsenic(V) solutions used in the experiments were prepared with reagent-grade KH_2AsO_4. Arsenic(III) solutions were prepared with reagent-grade As_2O_3. Arsenic standards for analytical purposes included solutions prepared with KH_2AsO_4, As_2O_3, and a commercial standard prepared for atomic absorption spectrophotometry (Fisher 1000 mg/L As from As_2O_3 in HNO_3).

The artificial groundwater employed in certain experiments was prepared from reagent-grade salts as described in Table 2 to approximate the natural conditions in which high arsenic concentrations would likely be encountered. Because of the tendency of $NaHCO_3$ to buffer solution in the alkaline region, and since much of the bicarbonate would be driven off as carbon dioxide at pH < 7, $NaHCO_3$ was not added to the acidic groundwater solutions. Instead,

additional NaCl and Na_2SO_4 were used to bring the total electrolyte concentrations to 15 meq/L, which was considered to be representative of a high TDS water in which arsenic might be found with competing anions.

Adjustment of pH was performed with reagent-grade HCl and NaOH.

Alcoa F-1 type activated alumina (Lot #1219623-20) used in the experiments was manually screened to mesh size 28x48 prior to experimental use (see Appendix A).

EQUIPMENT

All glassware used in these experiments was thoroughly washed with a commercially-prepared (Sparkleen) laboratory soap, an acid solution of two percent HNO_3, and was well rinsed with deionized water.

Batch tests were performed with an Eberbach horizontal shaker operated at approximately 15 5-cm excursions per minute.

Column test apparatus consisted of Nalgene 20-L polypropylene carboys connected to glass minicolumns by means of Nalgene PVC tubing (3/16" i.d. x 5/16" o.d.). The minicolumns (5 mm i.d. x 5 cm length) were constructed from CMS Pasteur minipipetes whose capillary ends were snapped off and fire-polished to form a rounded open tip. Flow through each minicolumn was controlled at the effluent end by means of Masterflex 5- and 10-channel pumps fitted with five #7013 and ten #7014 pumpheads, respectively. Effluent from each pumphead was collected in separate five-gallon glass or polycarbonate bottles. Operation of column test apparatus is illustrated and described below in the appropriate section.

The large volumes of solution required for the column tests were prepared in 20-L batches and mixed with a high-speed propeller mixer.

All samples were analyzed for arsenic with a Perkin-Elmer Model 372 Atomic Absorption Spectrophotometer fitted with an HGA-2200 graphite furnace, as described in the appendix. All pH measurements were made with Orion Research Model 501 digital analyzer fitted with a Fisher polymer body liquid-filled probe.

Reagents were weighed on a Mettler H31 analytical balance.

PROCEDURE

Batch Tests

Batch tests were performed to determine the equilibrium conditions between arsenic in the solid and liquid phases under a variety of conditions. The tests consisted of allowing different quantities of activated alumina to contact identical volumes and concentrations of arsenic solution. Control batches (blanks) contained only the arsenic solution, without alumina. Final arsenic concentrations were determined by atomic absorption spectrophotometry, and the difference between batch test and blank concentrations was attributed to adsorption of arsenic onto activated alumina.

TABLE 2. Makeup of Artificial Groundwater for Use in Arsenic(III) and Arsenic(V) Adsorption Experiments

pH	4-6		7-10	
TDS (mg/L)	1067		979	
Cations	mg/L	meq/L	mg/L	meq/L
Na^+	345	15	345	15
Anions				
Cl^-	266.2	7.5	177.5	5
HCO_3^-	--	--	305	5
SO_4^{2-}	367.5	7.5	240	5
TOTAL	633.7	15	722.5	15

Batch Test Number 1: Determination of Equilibrium Time

The procedure to determine the necessary shaking time to achieve equilibrium in batch tests was as follows:

1) 150-mL aliquots of nominal concentrations of 5 mg As(V)/L (pH 8) in an artificial groundwater were pipetted into 200-mL glass bottles.

2) To these bottles was added measured quantities (10 - 500 mg) of activated alumina. Duplicate batches were prepared for each concentration of activated alumina, as well as for the blanks.

3) Bottles were capped and placed on the shaker.

4) After 12 hours of shaking, one bottle from each set of duplicates was removed from the shaker, and its contents were decanted and filtered through a 0.45 ½m Millipore filter.

5) After 24 hours, the remaining bottles were removed, decanted, and filtered.

6) All samples were analyzed for arsenic and pH, and the results were recorded.

This procedure was repeated for batch tests in which duplicate samples were removed at two and four days, and seven and fourteen days. Data from these tests can be found in Appendix E. Results are presented in Figures 4 - 6.

Batch Test Number 2; Effect of Temperature on As(V) Adsorption

The test for the effect of temperature upon adsorption of arsenic(V) onto activated alumina commenced when it was observed that the metal body of the shaking apparatus became sensibly warmer during the course of the seven-day batch test. The temperature of the solution in the sample bottles was found to have risen from 25 to 38°C during the course of the first two days of shaking, but it remained fairly constant (± 2°C) for the duration of the test.

After the completion of the batch test at the elevated temperature, styrofoam insulation was added to the shaker, and a large box fan was installed to provide additional cooling (Fig. 1). This arrangement seemed to effectively dissipate heat created by the shaker, and the solution in the bottles remained near ambient temperature (25°C) during subsequent tests.

Solutions in the temperature studies consisted of 5 mg As(V)/L in an artificial groundwater at pH 6. The procedure followed was identical to that followed for the batch equilibrium tests, except that all bottles (duplicates and blanks) were removed, decanted, and filtered after seven days of shaking.

Data from the temperature tests can be found in Appendix A. Results are presented in Fig. 15.

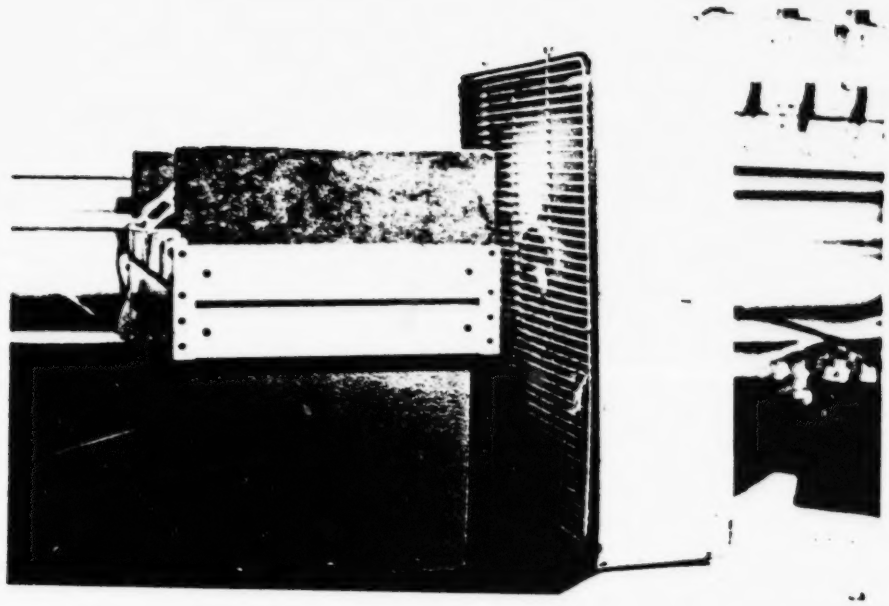

Figure 1. Batch apparatus including shaker and box fan for 25 °C equilibrium tests.

Batch Test Number 3: Effect of Chloride and Sulfate on As(V) Adsorption

In order to determine the effect of chloride and sulfate ion competition on the adsorption of As(V) onto activated alumina, batch tests were performed with four different background waters. Three of the four contained 5 mg As(V)/L in an electrolyte concentration of 15 meq/L, while the fourth contained only 5 mg As(V)/L in deionized water. The electrolyte solution compositions were as follows: 1) 7.5 meq/L NaCl (438 mg/L) and 7.5 meq/L Na_2SO_4 (540 mg/L); 2) 15 meq/L NaCl (876 mg/L); and 15 meq/L Na_2SO_4 (1064 mg/L).

The procedure for these batch tests was identical to that of the previous test, except that temperature was maintained at 25°C. All solutions were adjusted to pH 6, and time to equilibrium (t_{eq}) was seven days.

Data from the competition studies can be found in Appendix B. Results are presented in Fig. 16.

Column Tests

Column tests were developed to determine the maximum loading on the solid phase obtained at equilibrium with various liquid phase arsenic(V) concentrations. The condition of these tests was distinguished from that of the batch test, in that both the amount of alumina and the concentration of arsenic in the liquid phase were held constant. In the batch tests, by contrast, the concentration of arsenic in the liquid phase decreased as arsenic was adsorbed onto the alumina.

A column test consisted of an As(V) solution passed through a glass minicolumn containing a fixed amount of activated alumina. Effluent from the column was continuously sampled and collected until the effluent arsenic concentration reached 90 percent of the influent concentration, i.e., As(V) removal was reduced to < 10 percent. Total weight of arsenic removed was determined by the differences between influent and effluent arsenic concentrations multiplied by the volume of effluent collected. Loading upon the alumina was calculated by dividing the total weight of arsenic removed from solution by the weight of alumina in the column (usually 1.00 g).

The apparatus for the column tests was constructed so that the effluent could be sampled periodically without interrupting normal flow, and all the effluent could be continuously collected. To accomplish this, 20-L carboys containing the five different solutions to be adsorbed were placed on an elevated platform and connected to the minicolumns via plastic tubing attached with gum rubber hose connectors. Flow was controlled by variable speed peristaltic pumps which provided suction at the effluent end of the minicolumns and discharged into separate five-gallon glass or plastic bottles. T-connectors fitted with rubber hose and hose clamps on their open ends were inserted into the PVC tubing connecting the pumps to the bottles, to allow for intermittent sampling. A photograph of the apparatus and a detail of the minicolumns are presented in Figs. 2 and 3.

Operation of the columns included regular sampling, repeated preparation of influent solution, and measurement and sampling of collected effluent. Due to the relatively large volumes of solution involved, collected effluent

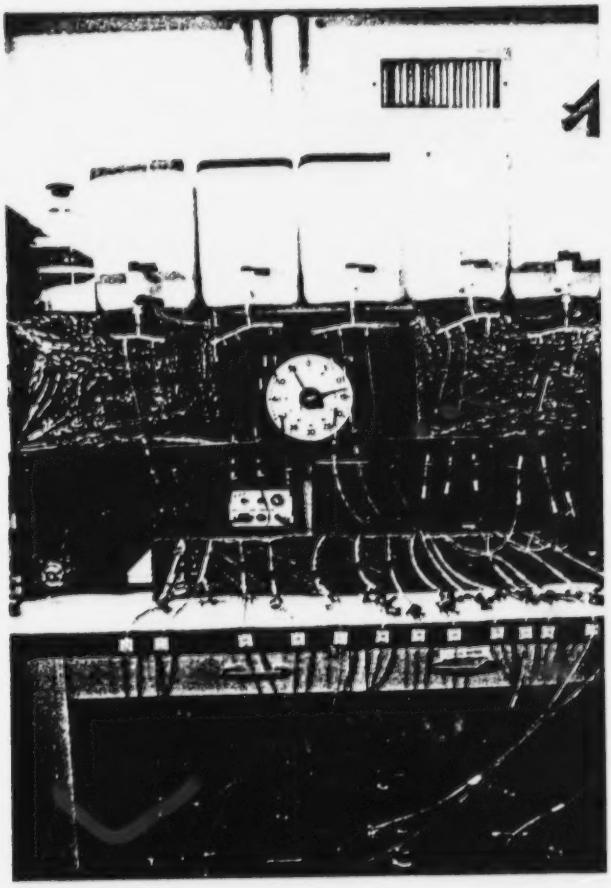

Figure 2. Column test apparatus.

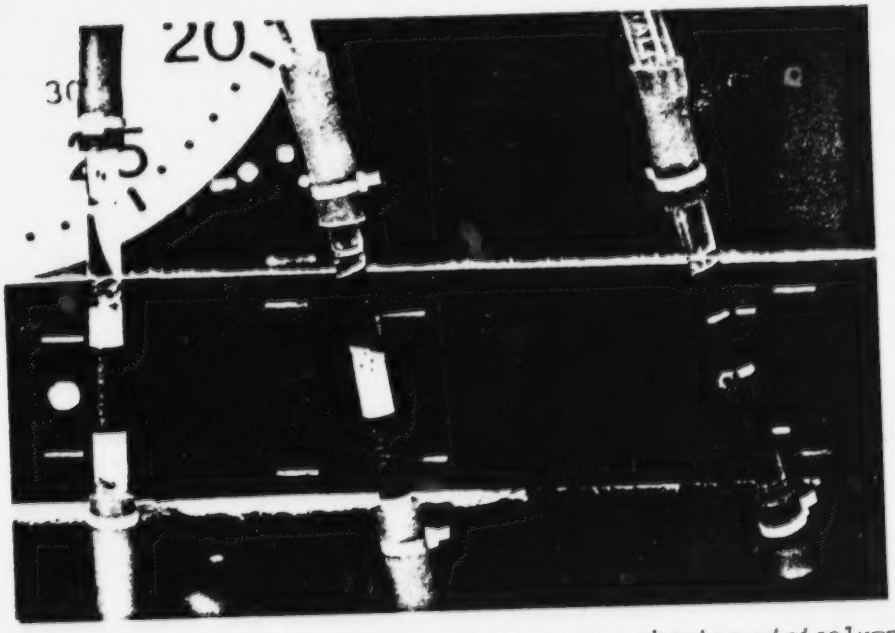

Figure 3. Detail of column test apparatus showing minicolumns.

volume was measured with a graduated cylinder; as the 20-L bottles were emptied, effluent samples were withdrawn at 4-L intervals until a total of 120 mL of effluent was collected from each five-gallon bottle. The alumina in the minicolumns was periodically reclassified by inversion to break up the alumina and prevent channeling and cementation of the top layers of the column.

Column Test Number 1: Optimization of pH

The first column test combined an investigation into the kinetics of minicolumn arsenic removal with the determination of the pH at which maximum adsorption occurs. Five different solutions were prepared with 1 mg As(V)/L in artificial groundwater adjusted to pH 5 - 9. Each carboy containing a different pH solution drained into three columns; two of the three columns continuned 1.00 g alumina supported on a glass wool plug, while the third column (the blank) contained only the glass wool.

Flow rate was maintained at 1 mL/min (± 0.1 mL/min), so that each carboy emptied in four to five days. Effluent was sampled daily during the first ten days, and every other day thereafter. An effluent history curve was developed for each pH, and calculations of arsenic loading based on that curve were compared with arsenic loading determined by As(V) concentrations of the effluent collected.

All minicolumns came to equilibrium within 20 days, and As(V) adsorption onto alumina was determined for each pH. Data from this test can be found in Appendix E. Results are presented in Figs. 7 and 14.

Column Test Number 2: Determination of Equilibrium Isotherm

A column test of adsorption at various concentrations of As(V) was developed to determine an equilibrium isotherm at optimum pH which could be compared to that determined by the batch test.

For this experiment, five different solutions were prepared with As(V) concentrations of 0.05, 0.10, 0.20, 0.50, and 1.00 mg/L in an artificial groundwater adjusted to pH 6. As in the previous test, solution was passed through the minicolumns until effluent As(V) concentration reached 90 percent of influent As(V) concentration.

Throughout the first 37 days of the experiment, flow rate was maintained at 1 mL/min. At that point, however, it was decided to increase the flow rate so that equilibrium would be attained more rapidly. Effluent concentrations of the minicolumns were measured at various flow rates from 1 to 5 mL/min, and the effect of increasing the flow rate was determined. From the 37th day through the duration of the column equilibrium test, flow rate was maintained at 4 mL/min.

Data from this test can be found in Appendix E. Results are presented in Figs. 8 and 9.

SECTION 4

RESULTS AND DISCUSSION

EQUILIBRIUM

The equilibrium isotherm is the relationship most often indicated to describe adsorption. In an equilibirum isotherm, different concentrations of adsorbate in the liquid phase are related to corresponding solid phase concentrations on the assumption that each correspondance represents an equilibrium condition at a constant temperature. While the various mathematical models which define isotherms (Langmuir, Freundlich, etc.) differ in their hypotheses concerning such physical characteristics as site energies and mono- or multilayer adsorption, any two points on a given isotherm are assumed to describe complete (or equally incomplete) adsorption reactions. However, the assumption of equilibrium becomes problematical with respect to the experimental method selected for the development of the isotherm.

Batch Test Equilibrium

Figures 4 and 5 compare As(V) isotherms developed from batch tests conducted under similar conditions for different lengths of time. As can be seen, the isotherm representing results of the 14-day test indicates significantly greater adsorption at each liquid phase concentration than either the 1- or 2-day tests (Fig. 4). In Fig. 5, on the other hand, isotherms obtained by 7- and 14-day tests appear to be in close agreement, indicating that most of the various concentrations of alumina have reached equilibrium with the arsenic within seven days. As a result, all subsequent batch test isotherms were generated by seven-day batch tests.

The same data, plotted in Fig. 6, presents percent removal as a function of time to equilibrium, emphasizing the extent to which arsenic loading at all concentrations increased with time. While this result was to be expected from the rate-limiting nature of certain time-dependent aspects of adsorption (such as diffusion), the approach to equilibrium did appear to be much slower than anticipated. Since increased solid phase concentration in batch tests corresponds to decreased liquid phase concentration, prolonged duration of the batch tests from one to fourteen days shifted the resultant equilibrium isotherms upward (in the direction of increased solid phase adsorption) and to the left (in the direction of lower liquid phase concentration).

Figure 6 also demonstrates that different adsorbent concentrations seem to approach equilibrium at different rates. For instance, the batch containing 80 mg alumina per 150 mL solution (0.533 g alumina/L) did not reach equilibrium until the seventh day, while the batch with 150 mg alumina (1.00

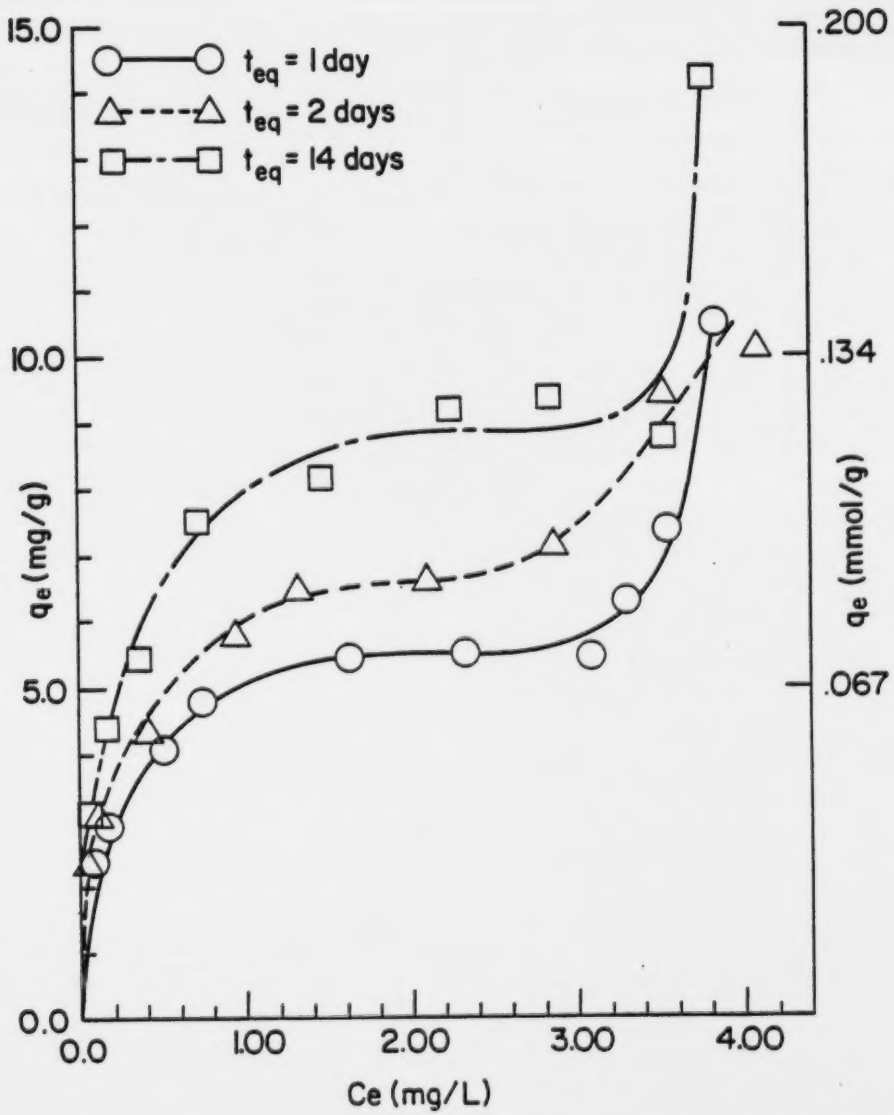

Figure 4. Comparison of 1-, 2-, and 14-day equilibrium isotherms for adsorption of arsenic(V) onto activated alumina.

(T=40 °C; C_o=5 mg As(V)/L; pH=8; TDS=1067 mg/L; Cl^-=5 meq/L; HCO_3^-=5 meq/L; SO_4^{2-}=5 meq/L)

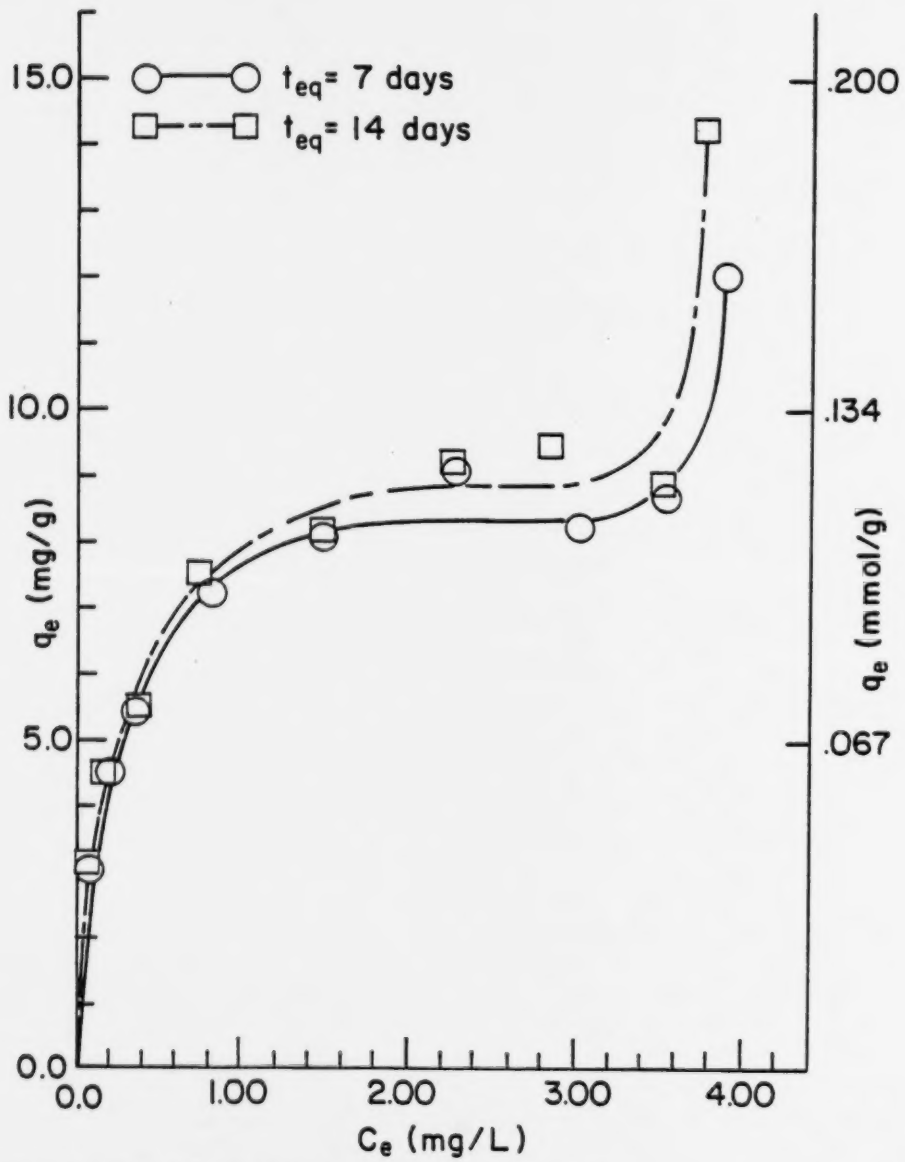

Figure 5. Comparison of 7- and 14-day equilibrium isotherms for adsorption of arsenic(V) onto activated alumina.

(T=40 °C; C_o=5 mg As(V)/L; pH=8; TDS=1067 mg/L; Cl^-=5 meq/L; HCO_3^-=5 meq/L; SO_4^{2-}=5 meq/L)

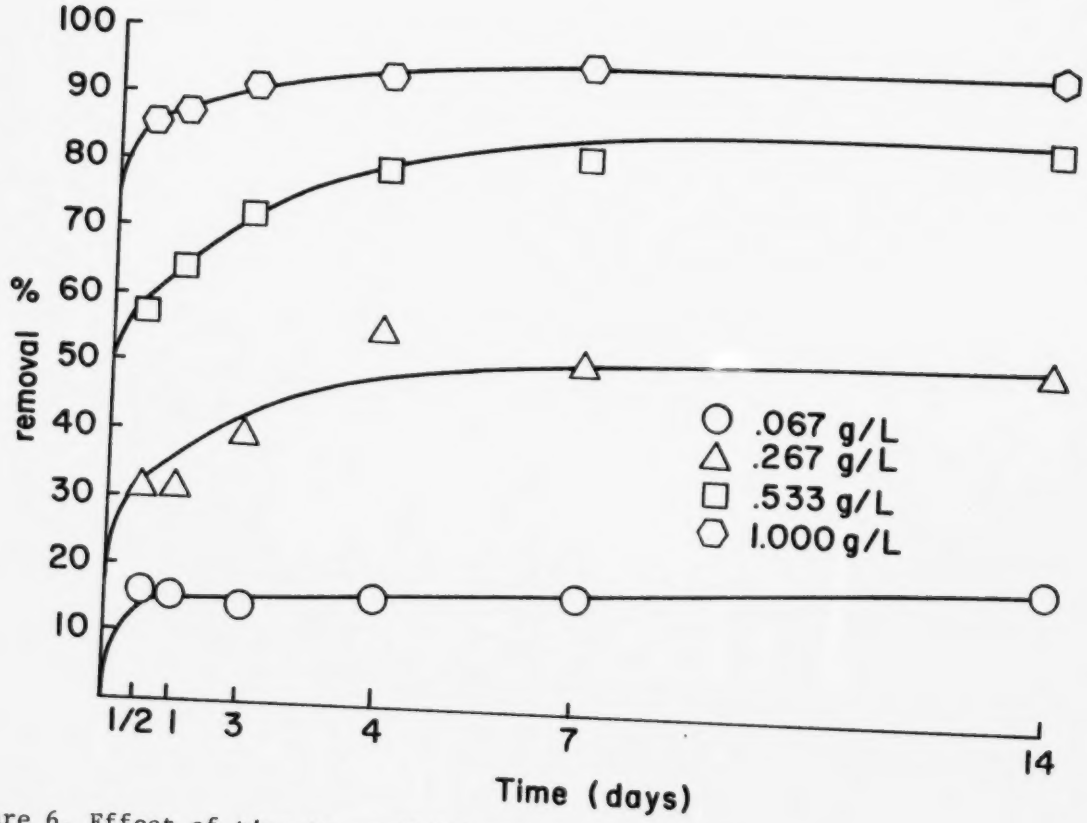

Figure 6. Effect of time to equilibrium on percent. removal of arsenic(V) by various concentrations of alumina.

(T=40 °C; C_o=5 mg As(V)/L; pH=8; TDS=1067 mg/L; Cl^-=5 meq/L; HCO_3^-=5 meq/L; SO_4^{2-}=5 meq/L)

mg alumina/L), reached equilibrium much more quickly.

The need to standardize variables in batch tests (e.g., time to equilibrium, initial adsorbate and adsorbent concentrations) becomes apparent when results from different experiments performed by researchers with different methods are compared. For example, Gupta and Chen [20] obtained an equilibrium value for As(V) adsorption from fresh water onto activated alumina of 4.9 mg As(V)/g alumina at a final concentration of 0.5 mg As(V)/L at pH = 6. By comparison, the present work reports a corresponding loading more than double that, of 10.5 mg As(V)/g alumina at the same pH. The lower values they reported, however, were obtained at an equilibrium time of only 36 hours, and the composition of the "fresh water" was unspecified.

Column Test Equilibrium

In the batch test, the initial liquid phase adsorbate concentration is uncharacteristically high--a matter of some concern in adsorption processes which tend to be irreversible (such as As(V) adsorption onto alumina). In contrast, the column test exposes a fixed amount of adsorbent to a constant concentration of adsorbate in the liquid phase. Equilibrium is indicated when the influent and effluent adsorbate concentrations are equal, i.e., the adsorbent is exhausted and no more adsorption occurs. Theoretically, the solid phase loading at equilibrium is independent of any rate-limiting steps; practically, however, intermediate effluent concentration is affected by the empty bed contact time (EBCT) of the solution in the column, and the approach to equilibrium may vary with the physical condition of the column.

Effluent concentration histories tracing the increase in effluent As(V) concentration over time for three columns at different pH are presented in Fig. 7. Feed solution to the columns contained 1.0 mg As(V)/L at pH 6, 7, and 9 in 15 meq/L TDS. Each column contained 1 g alumina in a volume of 1 mL, and the EBCT was approximately 1 minute. As expected, the curves of the columns closest to the optimum pH most closely approached the square wave pattern indicative of favorable adsorption without mass transfer limitation. The occurrence of breakthrough long before exhaustion can be accounted for by the relatively short column bed depth and EBCT, which increased the probability of both channeling and early breakthrough by advance of the adsorption zone.

Figure 8 compares the rate of uptake of As(V) by alumina to the flow rate at which the influent solution passes through the column for the influent concentrations of 0.50, 0.2, and 0.05 mg As(V)/L at pH 6. The figure indicates that a maximum uptake rate was attained for adsorption at the higher influent As(V) concentrations, while the column receiving the lowest As(V) concentration in the influent exhibited a nearly linearly increase in uptake rate. These results appear to provide evidence of a rate-limiting mass transfer step underlying the time-dependence of the adsorption reaction.

Batch Versus Column

Because of the complexity of the apparatus and the longer duration of the column tests at low adsorbate concentrations, batch tests are preferred for the laboratory determination of equilibrium isotherms--provided that the results are applicable to other equilibrium situations as well. The compari-

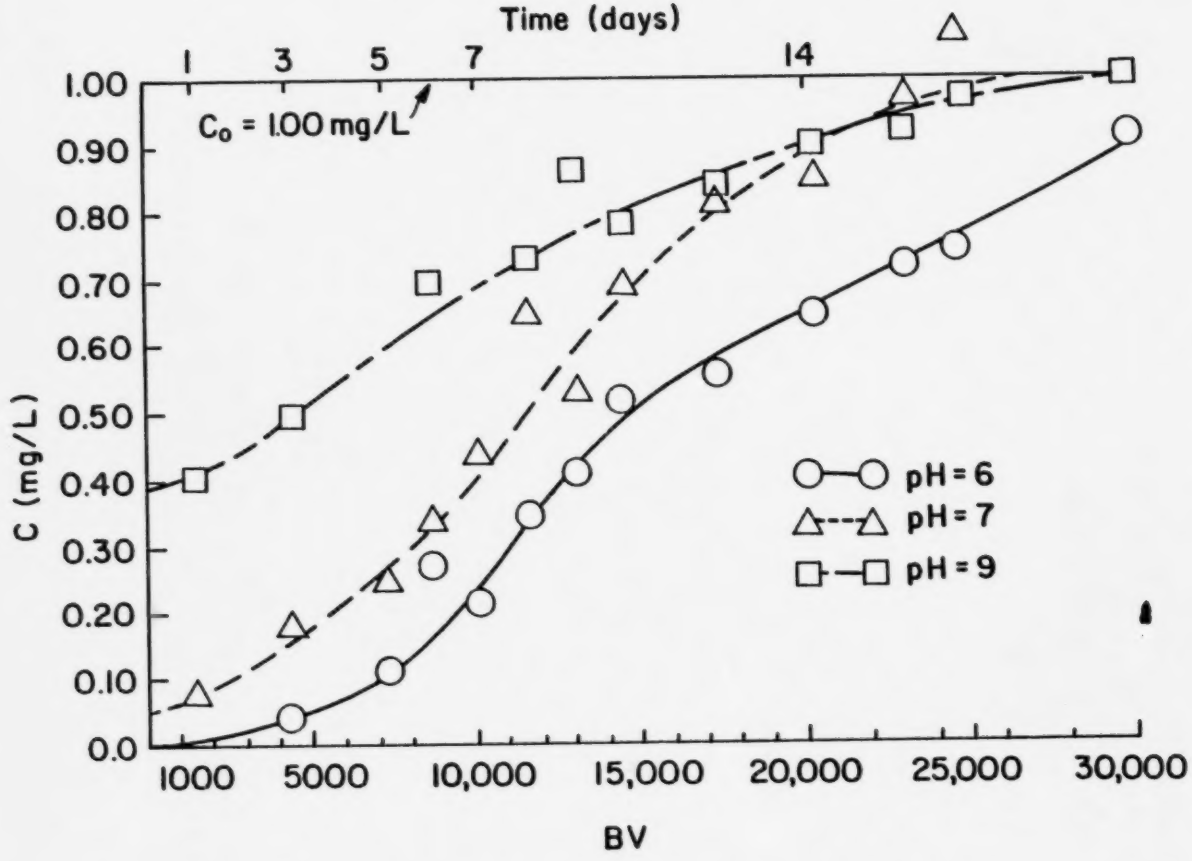

Figure 7. Effluent concentration histories for minicolumn adsorption of arsenic(V) onto activated alumina at pH 6, 7 and 9.

(C_o=1.0 mg As(V)/L; T=25 °C; TDS=1067 mg/L [pH 7,9] and 979 mg/L [pH 6])

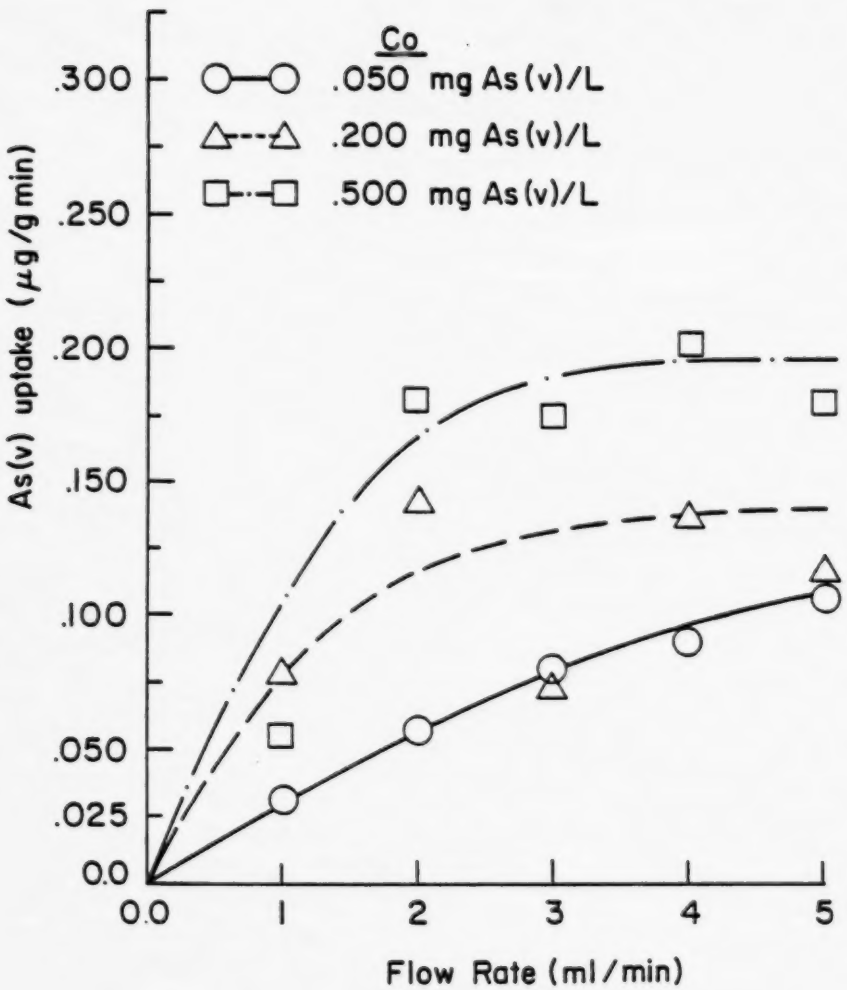

Figure 8. Effect of flow rate on rate of uptake of arsenic(V) by activated alumina.

(T=25 °C; pH=6; TDS=979 mg/L; Cl^-=7.5 meq/L; SO_4^{2-} = 7.5 meq/L)

son of equilibrium isotherm derived by both seven-day batch and minicolumn tests (Fig. 9) indicates that the results obtained by these methods agree very well at liquid phase equilibrium concentrations < 0.50 mg/L. However, the column isotherm predicts solid phase loadings progressively higher than those obtained by the batch test method. Data from which the figure was derived are presented in Tables E-2 and E-10.

One explanation for this divergence may be inferred from Figs. 4 and 5, which suggest that higher liquid phase arsenic concentrations require more time to reach equilibrium via the batch method. This implies that the higher loading obtained by the column test might be equalled by a batch test performed for some period of time longer than seven days.

Another aspect of As(V) removal by adsorption onto alumina in minicolumns which might have contributed to the higher solid phase loadings obtained is the considerable biological activity which occurred during the course of the column test. As might be expected during prolonged operation in an aqueous system open to the atmosphere, biological activity occurred to some extent in all columns in spite of the presence of up to 1.0 mg As(V)/L. This activity was first observed as a discoloration of the glass wool plugs, which turned brown and tended to darken with time. A crystal violet stain of a portion of the darkened material revealed the presence of significant bacterial growth, mostly by unidentified fibrous and rod-shaped organisms. in some cases, the discoloration extended to the alumina itself, which began to cake up into small clots which were not easily reclassified. It is unknown whether, or to what extent, these organisms contributed to the removal of As(V). Blank columns (containing no alumina) evidenced bacterial growth but did not exhibit any appreciable arsenic removal.

Originally it was believed that the higher initial liquid phase adsorbate concentration in the batch test would result in higher batch test loadings at equilibrium. This hypothesis was thought to be supported by the existence of a steeper concentration gradient between the solid and liquid phases at the surface of the alumina, which could increase the rate and extent of As(V) adsorption. Since adsorption of As(V) onto activated alumina is considered to be a relatively irreversible reaction, this increased rate of diffusion was expected to produce a higher solid phase loading at equilibrium. However, results indicate that, despite the higher initial As(V) concentration in the batch test, higher loadings did not occur.

Equilibrium Isotherms

Data from batch and column tests used to determine equilibrium isotherms in Fig. 9 are plotted according to the linearized forms of the Langmuir and Freundlich models in Figs. 10 - 13. Constants derived from these plots by the slope-intercept method are presented in Table 3.

Analysis of the linearized isotherms seems to support the contention of Hingston [30] that adsorption onto alumina generally conforms to the Langmuir model at low concentration, but does not reach a maximum. By inspection, it appears that the points plotted toward the right hand side of Figs. 10 and 11 (representing lower liquid phase arsenic concentrations) are indeed linear with respect to the Langmuir model. Statistically, the batch test data seem to correspond more closely to the linearized Langmuir model (r^2 = .99312).

TABLE 3. Linearized Isotherm Constants for Arsenic(V) Adsorption onto Activated Alumina at 25°C

Test	Langmuir (mmol)			Freundlich (mol)		
	Q	b	r^2	K	1/n	r^2
Column						
TDS	0.190	640	0.9632	70.9	0.421	0.9971
Batch						
TDS	0.192	612	0.9931	62.1	0.374	0.9408
DI H_2O	0.408	766	0.9305	167.5	0.272	0.9955

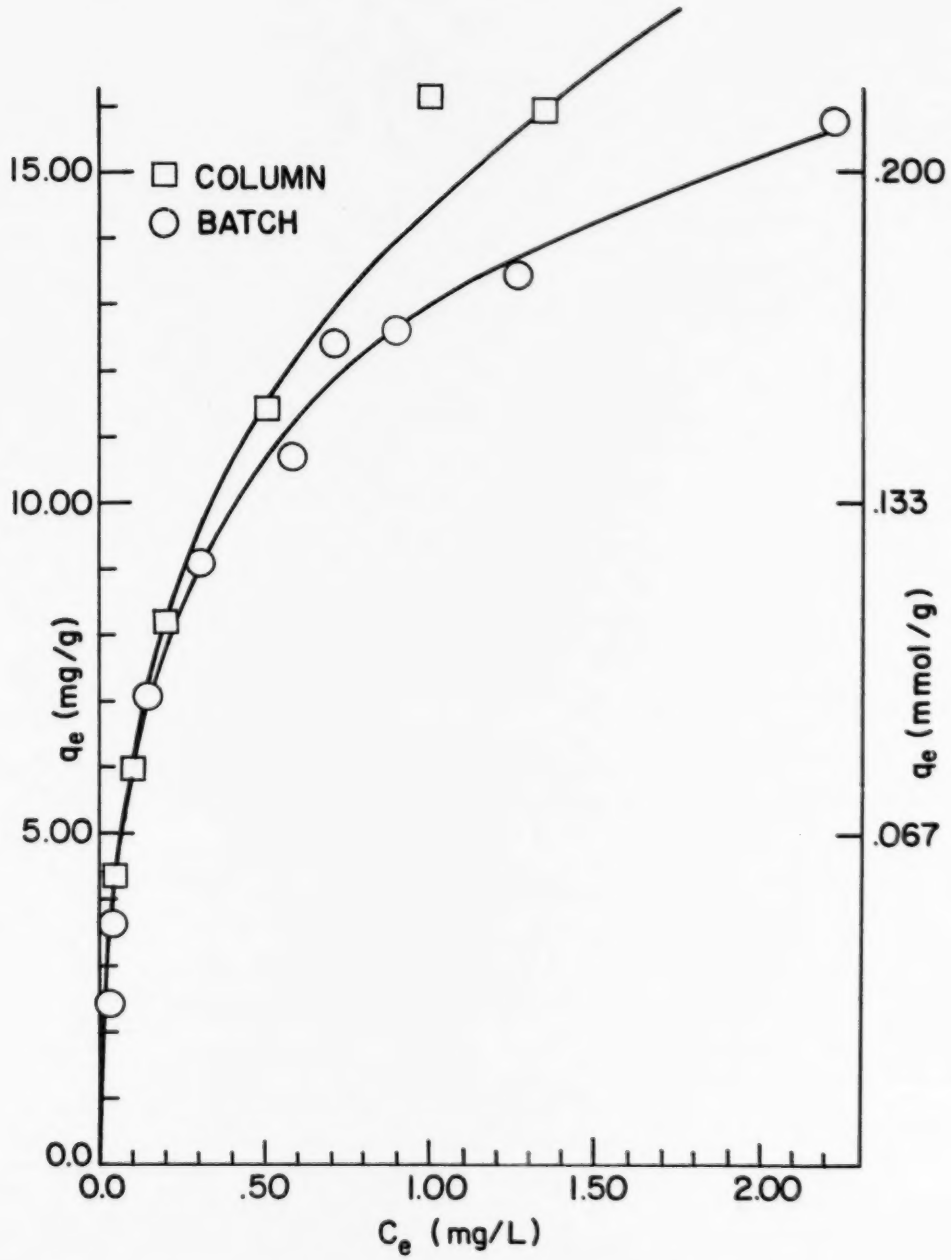

Figure 9. Comparison of equilibrium isotherms obtained by batch and column methods at optimum pH.

(T=25°C, pH=6; TDS=979 mg/L; Cl^-=7.5 meq/L; SO_4^{2-}=7.5 meq/L)

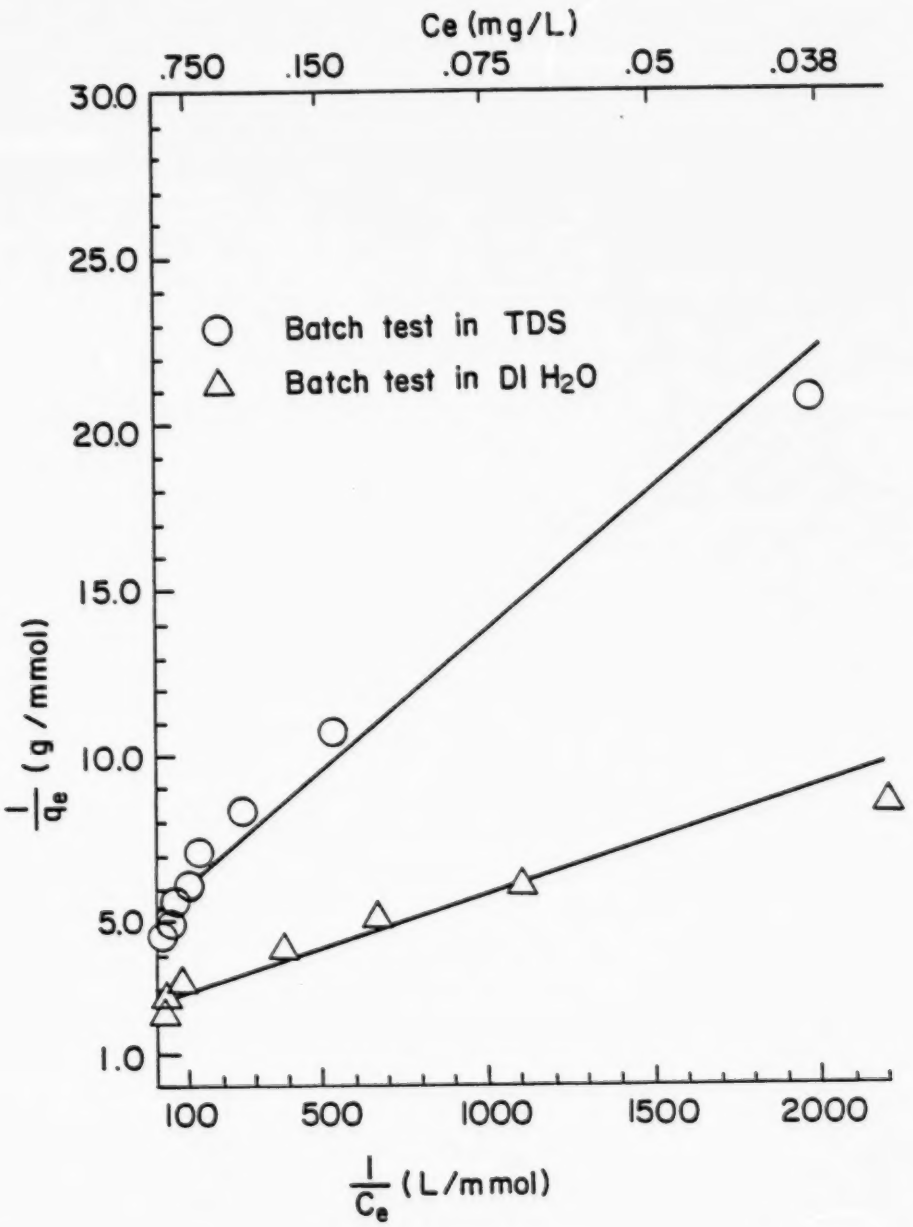

Figure 10. Linearized Langmuir isotherm for adsorption of arsenic(V) onto activated alumina by batch method at 25 °C.

(pH=6; C_o=5 mg As(V)/L; t_{eq}=7 days)

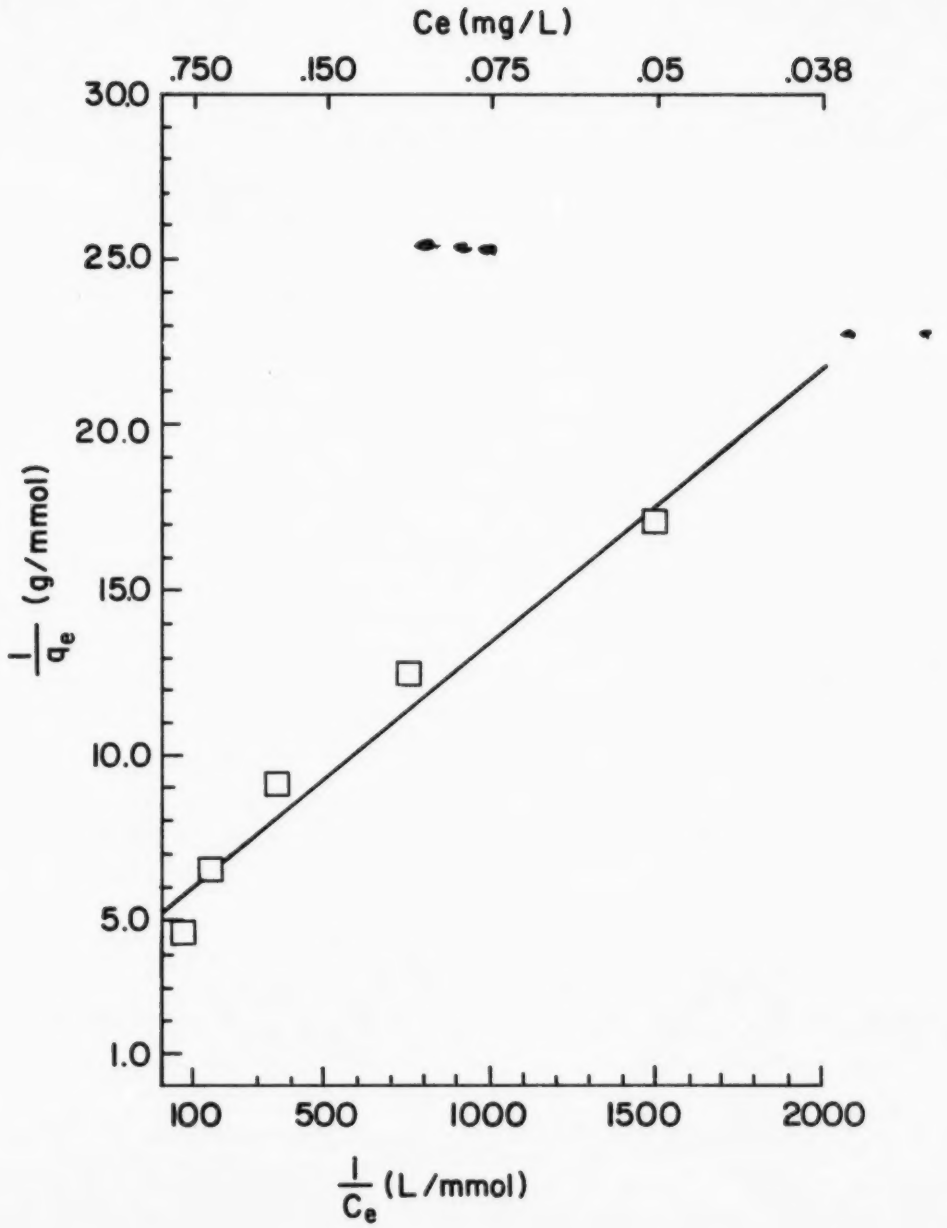

Figure 11. Lineraized Langmuir isotherm for adsorption of arsenic(V) onto activated alumina by column method at 25°C.

(pH-6; TDS=979 mg/L; Cl^-=7.5 meq/L; SO_4^{2-}=7.5 meq/L)

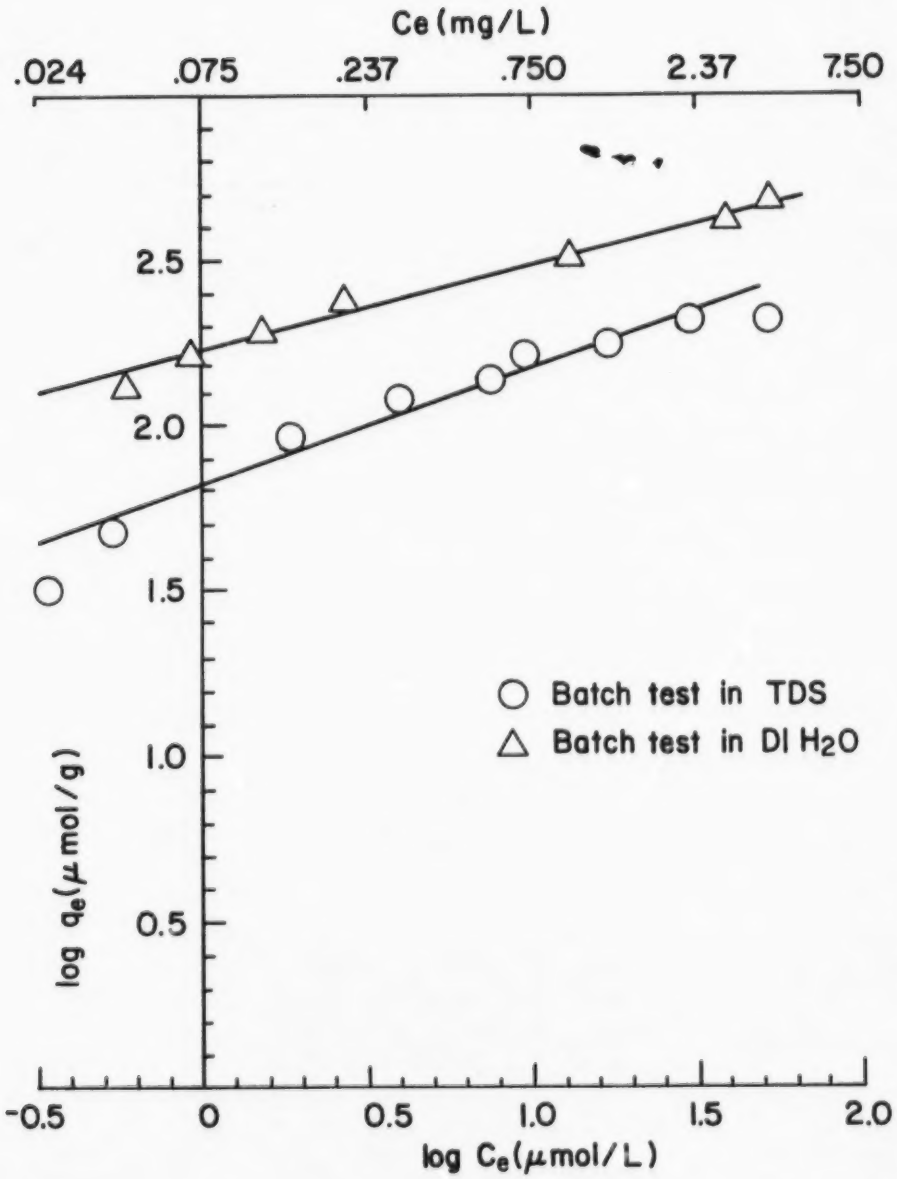

Figure 12. Linearized Freundlich isotherms for adsorption of arsenic(V) onto activated alumina by batch method at 25°C.

(C_o=5 mg As(V)/L; pH=6; t_{eq}=7 days)

However, the r^2 is biased by the extreme values and it is clear that the model yields results lower than batch test data (Fig. 9) at equilibrium concentrations less than 0.75 mg As(V)/L. The best fit of all (r^2 = .99712) was obtained by the column tests data compared with the linearized form of the Freundlich model (Fig. 13).

The significance of the Freundlich model with respect to As(V) adsorption onto activated alumina lies primarily in the assumption of heterogeneous site energies, which increase with increased adsorption. This assumption corresponds with the conclusions of Peri [27] concerning the different bond energies of hydroxide sites on the alumina surface.

It should be noted that, while the Langmuir model assumes monolayer adsorption, isotherms constructed from batch test data at pH 8 (Figs. 4 and 5) have a shape more characteristic of the BET model, which provides for multilayer adsorption at saturation. While the saturation concentration was apparently not reached by either batch or column tests at the optimum pH (pH = 6), commencement of multilayer coverage (C_s) at 3.7 mg As(V)/L at pH 8 indicates an area for further study.

ARSENIC ADSORPTION AND pH

Optimum pH for adsorption of As(V) onto activated alumina was determined by column tests with an influent concentration of 1.0 mg As(V)/L in an artificial groundwater at pH 5 - 9. Results were obtained by analysis of total effluent volume and confirmed by calculations based on daily effluent concentration and flow rate, and are presented in Fig. 14. The optimum pH for adsorption of As(V) onto activated alumina was pH 6.

This value is similar to those obtained by other researchers [20, 32]. According to the "adsorption envelope" theory discussed earlier, the optimum pH represents the point at which increased adsorption due to further formation of divalent arsenate ions is checked by a decrease in adsorption due to competition by hydroxyl ions. For arsenic acid,

$$pK_1 = 2.25$$

$$pK_2 = 6.77$$

$$pK_3 = 11.6 \qquad [36]$$

so it appears that a significant proportion of arsenate ions are adsorbed in the divalent form at the optimum pH.

Recently it has been suggested that protolyzable anions (such as arsenate) play a greater role in determining adsorption potential than was previously believed. In adsortion experiments involving electrophoretic mobility tests, Anderson and Malotky [37] concluded that adsorbed arsenate ions modify the electrokinetic behavior of alumina, resulting in greater electrochemical potential at certain pH than would otherwise be expected. They also contend that singly and doubly charged adsorbing ions have identical chemical adsorption energies, and that differentiation between monodentate and bidentate

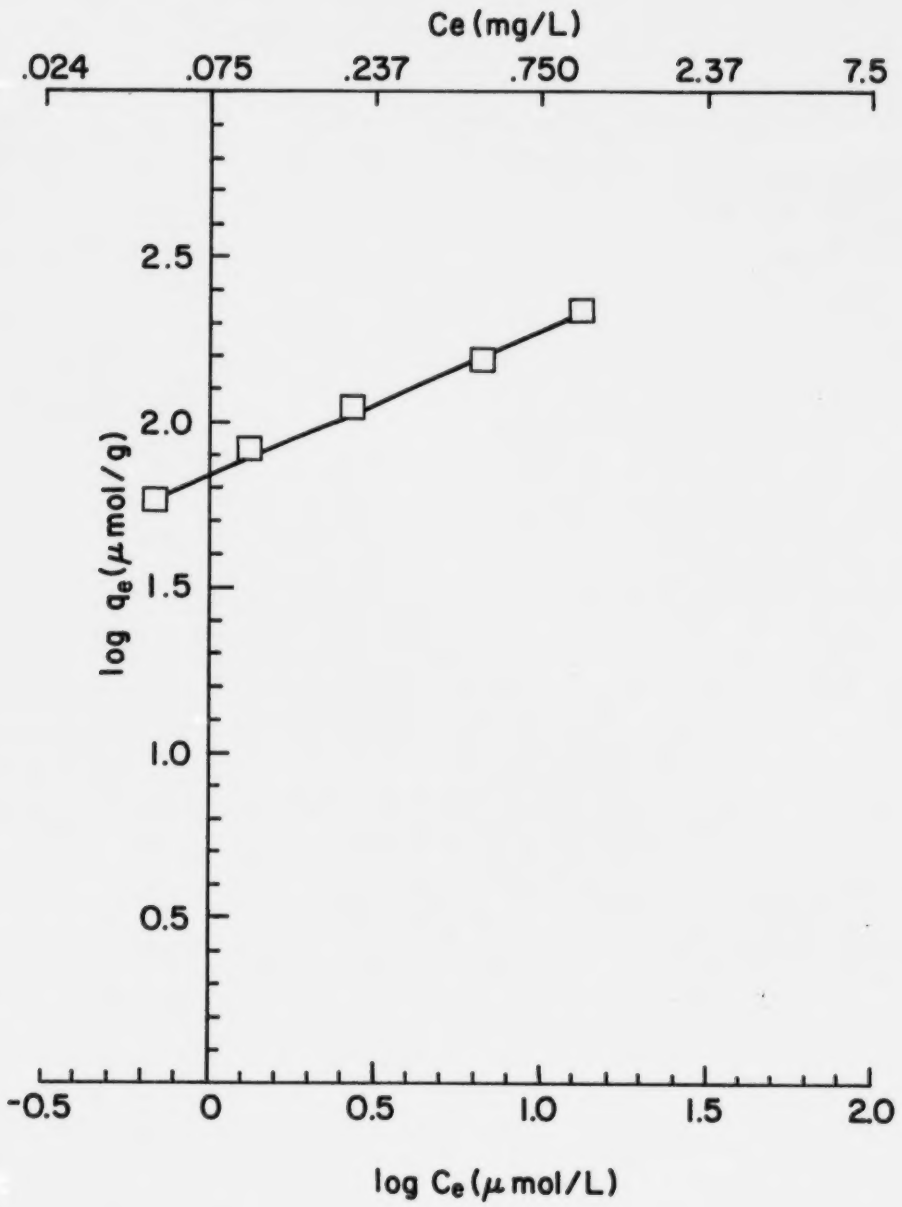

Figure 13. Linearized Freundlich isotherm for adsorption of arsenic(V) onto activated alumina by column method at 25°C.
(pH=6; TDS=979 mg/L; Cl^-=7.5 meq/L; SO_4^{2-}=7.5 meq/L)

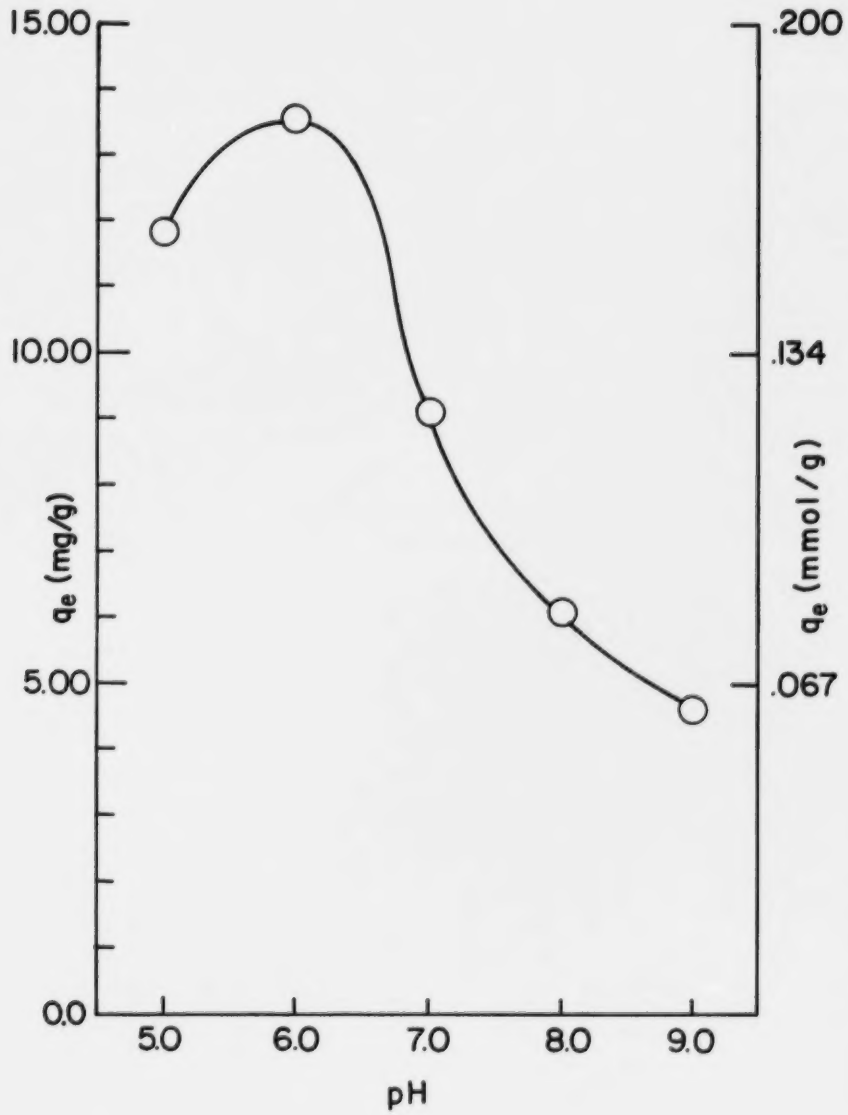

Figure 14. Effect of pH on adsorption of arsenic(V) onto activated alumina by column method.

(C_0 = 1 mg As(V)/L; TDS = 979 mg/L [pH 5, 6], and 1067 mg/L [pH 7 - 9])

sites is unnecessary.

ARSENIC ADSORPTION AND TEMPERATURE

Isotherms for adsorption of As(V) onto activated alumina at two different temperatures are presented in Fig. 15. As can be seen, arsenic adsorption increased when the temperature of the batch tests was raised from 25 to 40°C. This result appears to contradict the prevailing assumption that adsorption is an exothermic reaction, since an increase in temperature would then tend to drive the reaction in the direction of desorption from the solid phase.

One possible explanation for this apparent anomaly is that a higher temperature could increase the rate of diffusion into the solid phase and thus increase the solid phase loading at a given pH and time to equilibrium. This hypothesis is in agreement with findings of both batch and column tests that the adsorption reactions were controlled by kinetic constraints such as EBCT and time to equilibrium.

An alternate explanation is provided by Moilliet et al. [38] based on their review of the thermodynamics of adsorption. Concerning the change in free energy of adsorption, where

$$\Delta G = \Delta H - T\Delta S$$

they suggest that spontaneous adsorption may in some instances be considered an endothermic reaction (i.e., $\Delta H > 0$). In those cases, the negative free energy of adsorption for the reaction (including adsorbent, adsorbate, and solvent) would be provided by the entropic terms, ΔS. Thus, if overall ΔS increased significantly as oriented solvent molecules were displaced by the adsorbate, then the positive $T\Delta S$ term would be greater than the positive ΔH term, with the result that the free energy of adsorption would increase with temperature.

Verification of these hypotheses, as well as the determination of an optimum temperature for As(V) adsorption onto activated alumina, remains a subject for further research. In any case, these results suggest that practical consideration of activated alumina for arsenic removal include raw water temperature as a design criterion.

ARSENIC ADSORPTION AND ION COMPETITION

A comparison of equilibrium isotherms derived from batch tests of adsorption of As(V) onto activated alumina from solutions containing different concentrations of electrolytes (Fig. 16) indicates that arsenic adsorption was significantly reduced by anion competition. At an equilibrium concentration in the liquid phase of 1 mg As(V)/L, solid phase loading was reduced by 20 percent in the presence of 15 meq Cl^-/L (532.5 mg Cl^-/L), and by over 50 percent in the presence of 15 meq SO_4^{2-}/L (720 mg SO_4^{2-}/L), compared to adsorption in deionized water. Similarly, in an artificial groundwater composed of 7.5 meq/L each of chloride and sulfate ions, adsorption was reduced by over 40 percent.

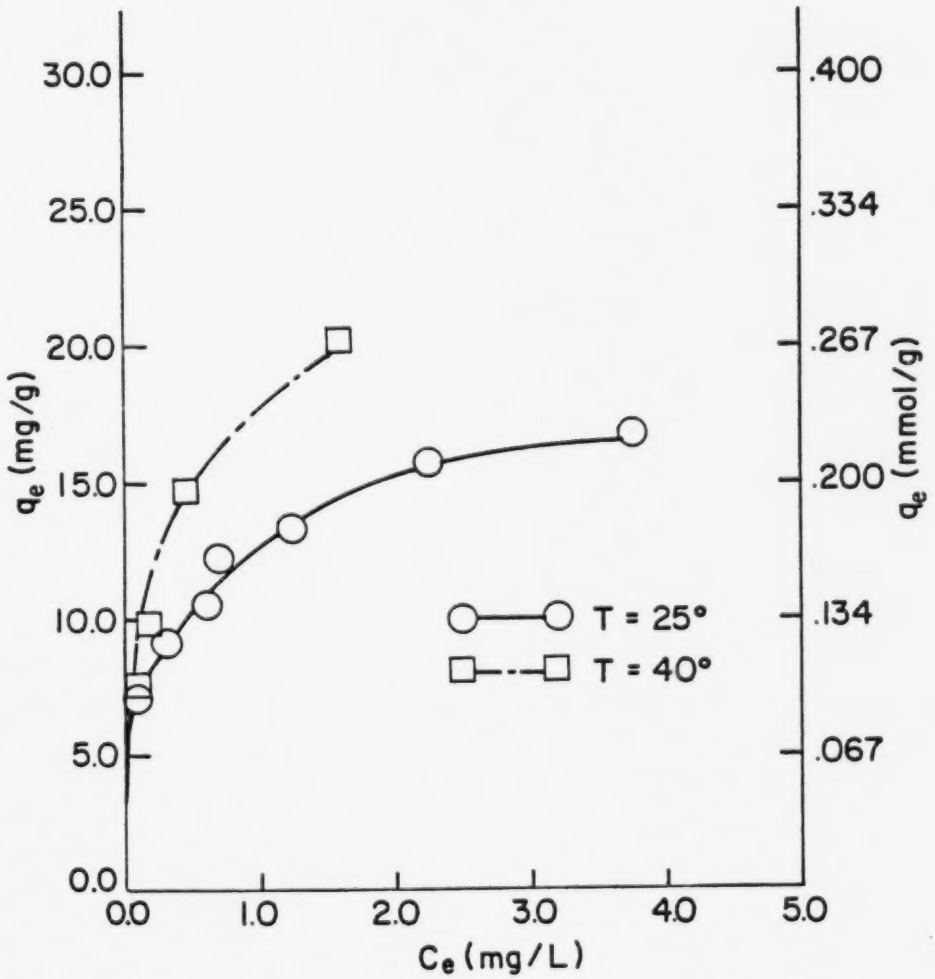

Figure 15. Effect of temperature on adsorption of arsenic (V) onto activated alumina by batch method.

(C_o=5 mg As(V)/L; pH=6; TDS=979 mg/L; Cl^-=7.5 meq/L; SO_4^{2-}=7.5 meq/L; t_{eq}=7 days)

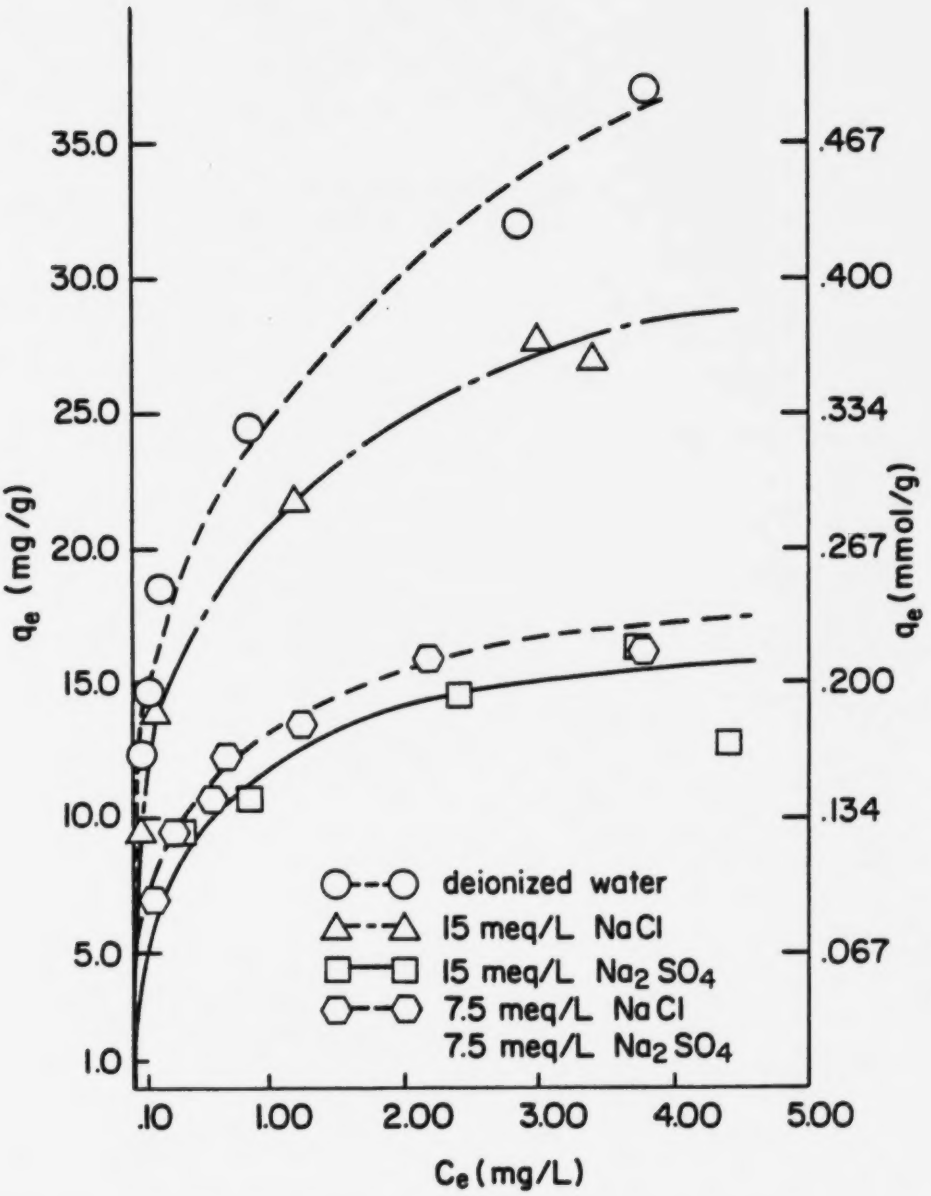

Figure 16. Effect of competition by chloride and sulfate ions on adsorption of arsenic(V) onto activated alumina.

(T=25 °C; C_o=5 mg As(V)/L; pH=6; t_{eq}=7 days)

These results are in agreement with the proposed selectivity series for competitive adsorption onto activated alumina [21], which predicts a greater reduction from sulfate competition than from chloride competition. However, the marked sensitivity of As(V) adsorption to competition from chloride ions was greater than expected on the basis of previous work with fluoride adsorption onto the same alumina [32].

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APPENDIX A

CONDITIONING ACTIVATED ALUMINA

Specifications for conditioning were designed on the basis of an assumed capacity of 0.5 meq acid or base/g alumina. A ten-fold stoichiometric excess was provided to overcome any kinetic constraints. Base and acid concentrations of 1% H_2SO_4 and 1% NaOH were selected to allow adequate exchange without promoting the deterioraton of the alumina.

Each glass conditioning column (2.1 cm i.d. x 40 cm length) was plugged with glass wool and filled with about 60 g alumina for a total settled bed volume of 50 mL. While the hydraulic contact time was theoretically set at two minutes, pump limitations increased detention time to 2.5 min. The conditioning column was backwashed with acid or base solution for several minutes prior to the start of each wash in order to insure uniform column behavior. The regime is described in Table A-1.

Following conditioning, all alumina was dried overnight at 105°C.

TABLE A-1. Sequence for Conditioning Activated Alumina

Base = 1% NaOH Q = 20 mL/min Acid = 1% H_2SO_4
Rinse = DI H_2O BV = 50 mL

Step	Solution	Volume (L)
1	Base	4.0
2	Rinse	2.4
3	Acid	4.0
4	Rinse	2.4
5	Base	4.0
6	Rinse	2.4
7	Acid	4.0
8	Rinse	7.2

APPENDIX B

ANALYSIS OF ARSENIC BY FLAMELESS ATOMIC ABSORPTION SPECTROPHOTOMETRY

Flameless atomic absorption spectrophotometry (FAAS) has yet to be recognized as a "standard method" for the determination of trace metals; it has been described in Standard Methods (15th Edition) [39] as a tentative method, however, and has for years been the method of choice for determination of trace quantities of arsenic in water [40-44].

The FAAS procedure followed during these experiments included use of a deuterium arc background corrector lamp, and involved high temperature charring (1100°C) of arsenic with an equal volume of 1000 mg $Ni(NO_3)_2$/L to prevent premature volatiliaton. Details of the procedure are listed in Table A-2.

All samples were run at least twice, and standards were retested periodically to check for changes in either slope or baseline of the calibration curve. Concentration values were derived by a combination of graphical and linear regression analysis involving at least three absorbance values at three separate concentrations.

The method of standard additions indicated a slight positive interference by the artificial groundwater solution. In order to compensate for this interference, all undiluted samples containing the electrolyte solution were tested against standards prepared from identical solutions. However, it was determined that dilution by a factor of ten times or more eliminated the interference, in which case the dilute samples were tested against standards prepared with deionized water.

TABLE B-1. Details of the Procedure for Arsenic Determination by FAAS

Equipment:	Perkin-Elmer Model 372 Atomic Absorption Spectrophotometer Perkin-Elmer Model HGA 2200 Graphite Furnace Perkin-Elmer Electrodeless Discharge Element Lamp (As) Perkin-Elmer Pyrolytically Coated Graphite Tubes Omniscribe Recorder Finn Micropipette (0.050 mL) Eppendorf Micropipette (0.050 mL)
Wavelength:	193.7 nm
Slit Width:	0.7 nm
Carrier Gas:	Argon
Gas Flow:	Normal
Dry:	30 sec at 105° C
Char:	25 sec at 1100° C
Atomize:	5 sec at 2500° C
Matrix:	1000 mg $Ni(NO_3)_2$/L
Matrix Volume:	0.050 mL
Sample Volume:	0.050 mL
Total Injection:	0.100 mL
Standards:	As_2O_3, KH_2AsO_4
Linear Range (mg/L):	0.001 - 0.100
Dilution Factor:	0 - 50X

APPENDIX C

RESULTS AND DISCUSSION OF ARSENIC(III) EXPERIMENTS

In addition to the laboratory studies of arsenic(V) adsorption, column tests were performed to determine the optimum pH for adsorption of arsenic (III) onto activated alumina. Apparatus and test procedure were identical to those of the arsenic(V) work, except that arsenic(III) was substituted for arsenic(V) and investigated over a range of pH 4-10.

The first column test covered pH 6-10, and reached 90 percent equilibrium in eight days (11,500 BV). Results indicated maximum adsorption at pH 6 at a loading much higher than that obtained by other researchers [20] (Fig. A-1). The second column test covering pH 4-8 ran for 14 days (20,000 BV) and, in contrast to the previous test, yielded an even higher maximum adsorption at an optimum pH 5. Furthermore, effluent history profiles exhibited marked irregularities which rendered the results questionable (Figs. A-1, A-2).

In order to verify the unusual results of the arsenic(III) column tests, an additional experiment was performed to check for the oxidation of test solutions from As(III) to As(V) by ion exchange separation (see Appendix D). These tests revealed that, in fact, substantial oxidation of As(III) in test solutions had occurred (Table A-5). As a result, further As(III) studies were postponed until an experimental technique which eliminated As(III) oxidation could be perfected.

The oxidation of As(III) to As(V) was not expected to occur under the relatively neutral pH conditions maintained in the column tests. Examination of the effluent history profile, however, suggests that oxidation may have occurred in the column, sometime between the fourth and tenth days of the run, corresponding to the periods of highest arsenic removal. That being the case, it is conceivable that biological activity contributed to the oxidation at that time; however, further studies are required to verify this hypothesis.

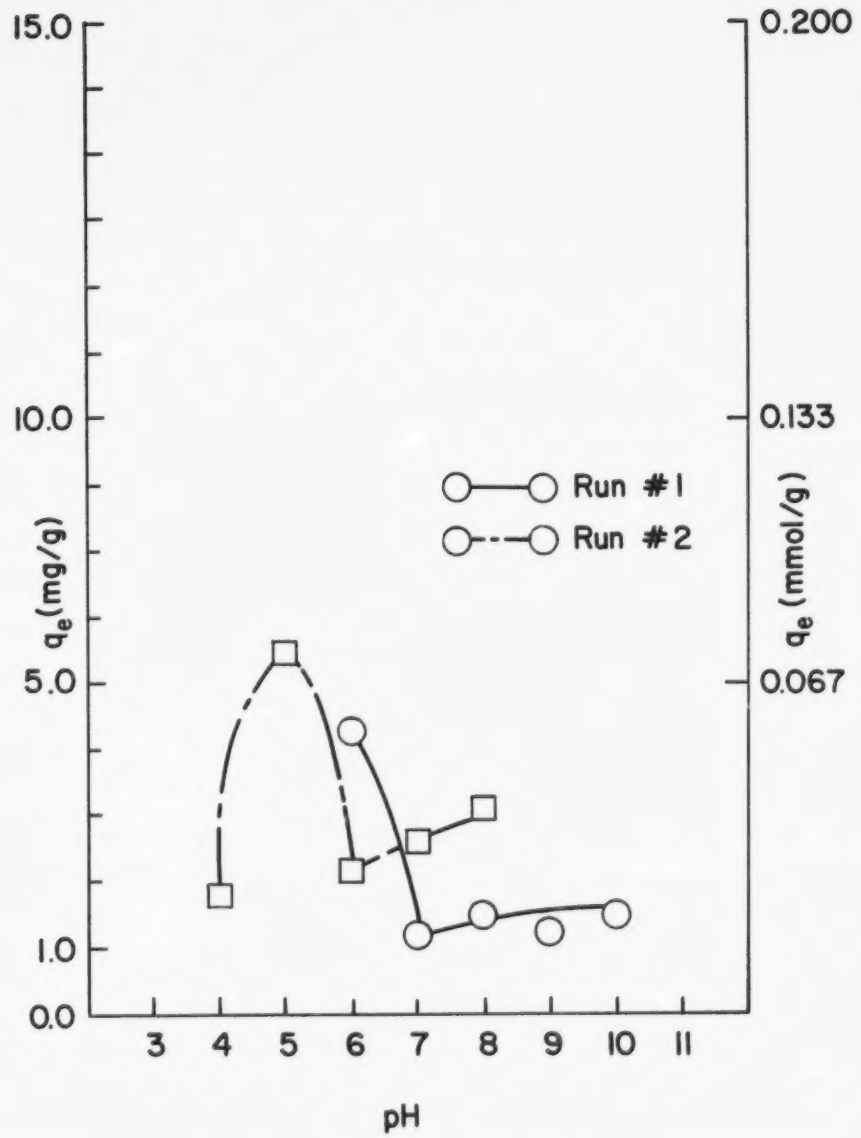

Figure A-1. Effect of pH on adsorption of an undetermined mixture of As(III) and As(V) onto activated alumina.

(C_o=1.0 mg As(V)/L; T-25°C; TDS=979 mg/L [pH 4-6] and 1067 mg/L [pH 7-10]

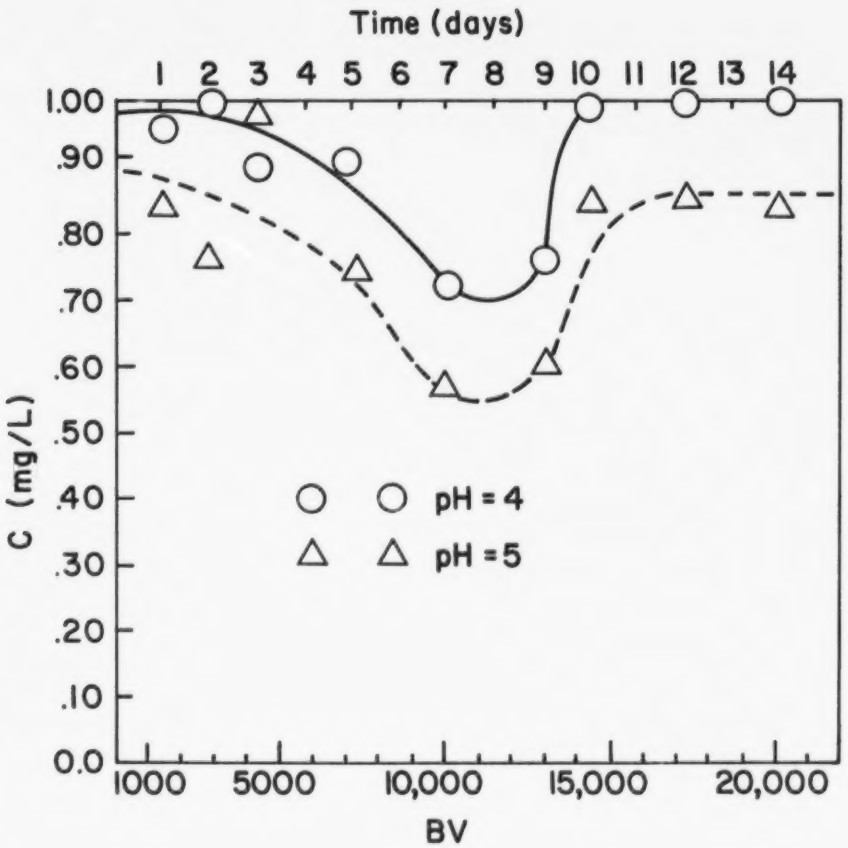

Figure A-2. Effluent concentration histories for minicolumn adsorption of an undetermined mixture of As(III) and As(V) onto activated alumina.

(C_o=1.0 mg As/L; T=25°C; TDS=979 mg/L; Cl^-=7.5 meq/L; SO_4^{2-}=7.5 meq/L)

APPENDIX D

ARSENIC(III) DETERMINATION BY ION EXCHANGE SEPARATION

Chromatographic techniques employing ion exchange resins have recently been applied to the separation of As(III) from As(V), replacing in many instances the older organic extraction methods [40-43].

The procedure followed in the test developed combined ion exchange separation of As(III) with detection of arsenic by FAAS, and involved three basic steps: 1) FAAS analysis of total arsenic; 2) removal of As(V) by ion exchange; and 3) FAAS analysis of remaining arsenic, presumably As(III). Arsenic(V) concentration was calculated as the difference between original and final arsenic concentrations.

The resin chosen for these tests was Amberlite IRA-458, a strong-base anion exchanger which had successfully removed As(V) in previous work. The resin was conditioned as described in Table A-3, and rendered in the chloride form.

Glass ion exchange columns (0.8 cm i.d. x 15 cm length) were filled with about 5 mL resin at a bed depth of approximately 10 cm. Flow rate was maintained at 1 mL/min, for a hydraulic detention time of 5 min. All solutions tested were standardized to approximately 1 mg/L total arsenic, and adjusted to pH 5-6.

As can be seen in Table A-4, virtually all (97.5 percent) of the As(V) was retained on the column, while 95 percent of the As(III) passed through. A standard composed of 0.500 mg As(III)/L and 0.500 mg As(V)/L was also used to check for As(III)/As(V) interference.

TABLE D-1. Conditioning Regime for IRA-458 Resin

Specifications

Bed Volume (BV): 130 mL

Resin Capacity: 1.3 meq/mL

Flow Rate: 20 mL/min

Conditioning Sequence

Step	Solution	Volume (L)	meq/mL
1	2 N HCl	1	10.0
2	0.002 N HCl	1	0.01
3	DI H_2O	0.5	-

TABLE D-2. Arsenic(III) Removal by IRA-458 Resin

Solution	C_o (mg As/L)	C_e (mg As/L)	Removal (1 %)
As(V) Standard	0.967	0.024	97.5
As(III) Standard	1.014	0.976	3.8
As(III/V) Standard	1.00[2]	0.490	51.0
Column 4[1]	1.014	0.400	60.5
Column 6	1.014	0.469	53.7
Column 8	1.014	0.404	60.2

[1]Column number indicates pH to which feed solutions were originally adjusted; however, all solutions were readjusted to pH 5-6 prior to ion exchange.

[2]0.500 mg As(III)/L + 0.500 mg As(V)/L

APPENDIX E

DATA FROM BATCH AND COLUMN TESTS

TABLE E-1. Adsorption of As(V) onto Activated Alumina by Batch Tests of Varying Durations

pH = 8 TDS = 1067 mg/L Cl^- = 5 meq/L HCO_3^- = 5 meq/L SO_4^{2-} = 5 meq/L

AA (g/L)	C_o (mg/L)	t_{eq} (days)	C_e (mg/L)	q_e (mg/g)	q_e (mmol/g)
0.067	4.525	0.5	3.80	10.9	.145
		1	3.82	10.5	.140
	4.75	2	4.08	10.1	.135
		4	4.00	11.2	.149
	4.70	7	3.90	12.0	.160
		14	3.75	14.2	.190
0.133	4.525	0.5	3.60	6.95	.092
		1	3.55	7.32	.098
	4.75	2	3.50	9.44	.125
		4	3.405	10.09	.134
	4.70	7	3.55	8.62	.115
		14	3.52	8.81	.118
0.200	4.525	0.5	3.35	5.90	.079
		1	3.28	6.26	.084
	4.70	7	3.05	8.25	.110
		14	2.82	9.38	.125
0.267	4.525	0.5	3.10	5.35	.071
		1	3.08	5.44	.072
	4.75	2	2.85	7.12	.095
		4	2.10	9.94	.132
	4.70	7	2.28	9.09	.120
		14	2.23	9.19	.123
0.400	4.525	0.5	2.40	5.32	.065
		1	2.32	5.50	.073
	4.75	2	2.10	6.60	.088
		4	1.35	8.50	.113
	4.70	7	1.48	8.06	.108
		14	1.45	8.12	.108

TABLE E-1 CONTINUED

AA (g/L)	C_o (mg/L)	t_{eq} (days)	C_e (mg/L)	q_e (mg/g)	q_e (mmol/g)
0.533	4.525	0.5	1.92	4.88	.059
		1	1.62	5.44	.072
	4.75	2	1.30	6.47	.086
		4	.963	7.10	.095
	4.70	7	.825	7.27	.097
		14	.700	7.50	.100
0.667	4.75	2	.90	5.78	.077
		4	.70	6.08	.081
0.800	4.525	0.5	1.00	4.41	.050
		1	.725	4.75	.063
	4.70	7	.37	5.41	.072
		14	.36	5.42	.072
1.00	4.525	0.5	.640	3.89	.052
		1	.510	4.02	.054
	4.75	2	.41	4.34	.057
		4	.29	4.46	.059
	4.70	7	.19	4.50	.060
		14	.155	4.54	.061
1.50	4.525	0.5	.310	2.81	.038
		1	.190	2.90	.038
	4.75	2	.11	3.10	.041
		4	.092	3.11	.042
	4.70	7	.076	3.08	.041
		14	.074	3.08	.041
2.00	4.525	0.5	.190	2.28	.030
		1	.107	2.32	.031
	4.75	2	.084	2.34	.031
		4	.050	2.35	.031
	4.70	7	.038	2.33	.031
		14	.031	2.33	.031
2.667	4.525	0.5	.083	1.66	.022
		1	.069	1.67	.022
	4.75	2	.043	1.76	.024
		4	.029	1.77	.024
	4.70	7	.028	1.75	.022
		14	.012	1.76	.024

TABLE E-1 CONTINUED

AA (g/L)	C_o (mg/L)	t_{eq} (days)	C_e (mg/L)	q_e (mg/g)	q_e (mmol/g)
3.333	4.525	0.5	.096	1.40	.019
		1	.040	1.43	.019
	4.75	2	.041	1.41	.019
		4	.026	1.42	.019
	4.70	7	.012	1.41	.019
		14	.008	1.41	

TABLE E-2. Adsorption of Arsenic(V) onto Activated Alumina at 25°C by Batch Test

C_o = 5 mg As(V)/L; pH = 6; TDS = 979 mg/L; Cl^- = 7.5 meq/L; SO_4^{2-} = 7.5 meq/L; t_{eq} = 7 days

Sample[1]	Alumina (g/L)	C_e (mg/L)	C (mg/L)	q_e (mg/g)	q_e (mmol/g)
300A	2.00	0.032	4.82	2.41	0.032
300B	2.00	0.18	4.83	2.52	0.032
200A	1.33	0.040	4.81	3.61	0.048
200B	1.33	0.035	4.81	3.61	0.048
100A	0.667	0.139	4.71	7.06	0.094
100B	0.667	0.136	4.71	7.07	0.094
75A	0.500	0.270	4.58	9.16	0.122
75B	0.500	0.312	4.54	9.07	0.121
60A	0.400	0.664	4.18	10.47	0.139
60B	0.400	0.495	4.35	10.88	0.145
50A	0.333	0.751	4.10	12.28	0.164
50B	0.333	0.656	4.19	12.58	0.168
40A	0.267	1.33	3.52	13.20	0.176
40B	0.267	1.20	3.65	13.69	0.183
25A	0.167	2.15	2.70	16.20	0.216
25B	0.167	2.28	2.57	15.4	0.203
10A	0.067	3.64	1.21	18.20	0.243
10B	0.067	3.90	0.94	14.20	0.190
0A	0.000	4.80			
0B	0.000	4.89			

[1]Sample number indicates mg alumina/150 mL sample and letter designating duplicate.

TABLE E-3. Adsorption of Arsenic(V) onto Activated Alumina at 40°C by Batch Test

C_o = 5 mg As(V)/L, pH = 6; TDS = 979 mg/L, Cl^- = 7.5 meq/L; SO_4^{2-} = 7.5 meq/L, t_{eq} = 7 days

Sample[1]	Alumina (g/L)	C_e (mg/L)	C (mg/L)	q_e (mg/g)	q_e (mmol/g)
300A	2.00	0.029	4.97	2.48	0.034
300B	2.00	0.017	4.98	2.49	0.032
200A	1.33	0.032	4.97	3.73	0.050
200B	1.33	0.028	4.97	3.73	0.050
100A	0.667	0.120	4.88	7.32	0.098
100B	0.667	0.097	4.90	7.35	0.098
75A	0.500	0.185	4.82	9.63	0.128
75B	0.500	0.186	4.81	9.63	0.128
50A	0.333	0.480	4.52	13.56	0.181
50B	0.333	0.452	4.55	13.64	0.182
25A	0.167	1.492	3.51	21.05	0.281
25B	0.167	1.794	3.21	19.24	0.257
0A	0.000	4.98			
0B		5.01			

[1]Sample number indicates mg alumina/150 mL sample and letter designating duplicate.

TABLE E-4. Adsorption of Arsenic(V) onto Activated Alumina in Deionized Water by Batch Test

C_o = 5 mg As(V)/L pH = 6 t_{eq} = 7 days T = 25°C

Sample[1]	Alumina (g/L)	C_e (mg/L)	C (mg/L)	q_e (mg/g)	q_e (mmol/g)
300A	2.00	0.004	5.02		
300B	2.00	0.004	5.02	2.5[2]	0.03[2]
200A	1.33	0.003	5.02		
200B	1.33	0.002	5.02	3.76[2]	0.05[2]
100A	0.667	0.014	5.01	7.52	0.100
100B	0.667	0.014	5.01	7.52	0.100
75A	0.500	0.033	4.99	9.98	0.133
75B	0.500	0.035	4.99	9.98	0.133
60A	0.400	0.068	4.96	12.40	0.166
60B	0.400	0.069	4.96	12.40	0.166
50A	0.333	0.123	4.90	14.71	0.196
50B	0.333	0.100	4.92	14.77	0.197
40A	0.267	0.182	4.84	18.13	0.242
40B	0.267	0.210	4.82	18.05	0.241
25A	0.167	0.948	4.08	24.43	0.326
25B	0.167	0.926	4.10	24.55	0.328
10A	0.067	2.94	2.08	31.04	0.414
10B	0.067	2.83	2.20	32.84	0.438
5A	0.033	3.70	1.32	40.00	0.534
5B	0.033	3.88	1.14	34.54	0.461
0A	0.000	5.05			
0B	0.000	5.00			

[1]Sample number indicates mg alumina/150 mL sample and letter designating duplication

[2]Results indicate complete adsorption of arsenic in sample solution

TABLE E-5. Adsorption of Arsenic(V) onto Activated Alumina in High Sulfate Water by Batch Test

C_o = 5 mg As(V)/L TDS = 1065 mg/L SO_4^{2-} = 15 meq/L
pH = 6 T = 25°C t_{eq} = 7 days

Sample[1]	Alumina (g/L)	C_e (mg/L)	C (mg/L)	q_e (mg/g)	q_e (mmol/g)
75A	.500	.335	4.50	9.00	.120
75B	.500	.364	4.47	8.94	.119
50A	.333	.971	3.86	11.59	.155
50B	.333	.923	3.91	11.74	.156
25A	.167	2.46	2.37	14.23	.190
25B	.167	2.38	2.45	14.67	.196
10A	.067	3.88	.955	14.25	.190
10B	.067	3.61	1.22	18.21	.243
5A	.033	4.40	.435	13.18	.176
5B	.033	4.42	.415	12.58	.168
0A	.000	5.10			
0B	.000	4.56			

[1]Sample number indicates mg alumina/150 mL sample and letter designating duplicate.

TABLE E-6. Adsorption of Arsenic(V) onto Activated Alumina in High Chloride Water

C_o = 5 mg As(V)/L, pH = 6; TDS = 877.5 mg/L, t_{eq} = 7 days; Cl^- = 15 meq/L, T = 25°C

Sample[1]	Alumina (g/L)	C_e (mg/L)	C (mg/L)	q_e (mg/g)	q_e (mmol/g)
75A	0.500	0.042	4.76	9.52	0.127
50A	0.333	0.170	4.63	13.89	0.185
50B	0.333	0.178	4.62	13.87	0.185
25A	0.167	1.08	3.72	22.32	0.298
25B	0.167	1.31	3.49	20.94	0.279
10A	0.067	2.98	1.82	27.16	0.362
10B	0.067	2.92	1.88	28.06	0.374
5A	0.033	4.12	0.68	20.61	0.275
5B	0.033	3.68	1.12	33.94	0.453
0A	0.000	4.73			
0B	0.000	4.87			

[1]Sample number indicates mg alumina/150 mL sample and letter designating duplicate.

TABLE E-7. Daily Effluent Concentrations from Mini-Column Tests to Determine Optimum pH for Adsorption of As(V) onto Activated Alumina
C_o = 1.00 mg As(V)/L TDS = 979 mg/L at pH = 5 and 6 and 1067 mg/L at pH 7 - 9

	pH = 5		pH = 6	pH = 7		pH = 8		pH = 9	
Day	#1	#2	#1	#1	#2	#1	#2	#1	#2
1				.058	.095				.402
3	.137	.163	.045	.212	.145	.343	.417	.512	.475
5	.337	.337	.102	.231	.254	.409	.437		
6	.438	.482	.270	.303	.370	.584	.560	.683	.700
7	.459	.506	.207	.369	.508	.665	.662		
8	.605	.639	.344	.612	.679	.811	.816	.603	.856
9	.624	.634	.404	.468	.588	.933	.937	.808	.923
10	.710	.685	.516	.645	.737	.789	.780		.784
12	.787	.767	.555	.749	.890	.879	.894	.885	.787
14	.850	.762	.647	.845	.863	.890	.986	.944	.864
16	.840	.854	.714	.950	.997	.901	.941	.931	.921
17	.898	.884	.748	1.026	1.061	.955	.953	.987	.968
20	.936	.984	.912			.882	.903	.971	1.060

TABLE E-8. Range and Average Daily Effluent Concentations of Blank Minicolumns in As(V) pH Optimization Tests
C_o = 1.00 mg As(IV)/L
TDS = 979 mg/L at pH 5, 6 and 1067 mg/L at pH 7, 8, 9

pH	C_{AVG} (mg/L)	C_{MIN} (mg/L)	C_{MAX} (mg/L)
5	.981	.926	1.020
6	.980	.956	1.038
7	.950	.880	1.040
8	.955	.894	1.032
9	.973	.864	1.099

TABLE E-9. Adsorption of Arsenic(V) onto Activated Alumina at Varying pH by Column Test

C_o = 1 mg As(V)/L
TDS = 979 mg/L (pH 5, 6)
1067 mg/L (pH 7-9)

Column[1]	T[2] (mg/mg)	BV to Equilibrium x 10^{-3}	C/C_o (%)	q_e[3] (mg/g)	q_e[4] (mmol/g)	Deviation[5] (%)
5-1	2.48	28.9	94	11.64	10.0	-15
5-2	2.42	29.0	98	11.96		
6-1	1.68	24.7	91	14.66	16.0	10
6-2	4.21	52.1	99	12.38		
7-1	2.41	22.5	100	9.33	11.1	22
7-2	3.24	28.5	100	8.80		
8-1	4.24	26.1	92	6.15	7.0	15
8-2	4.20	25.4	92	6.04		
9-1	6.64	24.5	97	3.69	5.5	15
9-2	4.97	29.0	100	5.83		

[1]Column number indicates pH of influent and number designating blank (0) or duplicate (1, 2)

[2]See Symbols and Abbreviations

[3]q_e determined frm concentration of accumulated effluent volume

[4]q_e determined from integration of area between breakthrough curve and influent As(V) concentration (1.0 mg/L)

[5]Deviation determined between average q_e values

TABLE E-10. Adsorption of Arsenic(V) onto Activated Alumina by Column Method at Various Influent As Concentrations

pH = 6 Cl^- = 5 meq/L T = 25°C
TDS = 979 mg/L SO_4^{2-} = 5 meq/L

Column[1]	T[2] (mg/mg)	BV to Equilibrium x 10^{-3}	C/C_o (%)	q_e (mg/g)	q_e (mmol/g)
1000-1	3.81	61.5	95.7	16.13	0.215
1000-2	4.03	65.3	95.0	16.21	0.216
500-1	7.57	80.2	95.9	10.59	0.141
500-2	5.97	73.0	94.0	12.23	0.163
200-1	10.8	86.6	95.2	8.02	0.107
200-2	11.4	94.9	92.6	8.34	0.111
100-1	22.9	137.3	91.1	6.00	0.080
100-2	21.8	133.0	86.7	6.10	0.081
50-1	65.8	289.5	86.9	4.40	0.059

[1]Column number indicates influent As(V) concentration (g/mL) and number designating blank (0) or duplicate (1, 2).

[2]See Symbols and Abbreviations

TABLE E-11. Variation of Arsenic(V) Uptake Rate with Influent Flow Rate

pH = 6 Cl^- = 7.5 meq/L T = 25°C
TDS = 979 mg/L SO_4^{2-} = 7.5 meq/L
(Samples taken at BV = 53.3×10^3)

C_o (mg/L)	As(V) Uptake Rate (µg/g min)				
	1 mL/min	2 mL/min	3 mL/min	4 mL/min	5 mL/min
.500	.056	.180	.174	.200	.180
.200	.077	.142	.072	.136	.115
.100	.065	.130	.198	.248	.320
.050	.030	.056	.078	.084	.105

TABLE E-12. Adsorption of Arsenic(III) and Arsenic(V) in an Undetermined Mixture onto Activated Alumina at Varying pH

C_o = 1 mg As/L
TDS = 979 mg/L

Cl^- = 7.5 meq/L
SO_4^{2-} = 7.5 meq/L

pH	Test Number	C/C_o (%)	q_e (mg/g)	q_e (mmol/g)
4	1	100.0	1.80	0.024
5	1	90.1	5.46	0.073
6	1	94.4	2.16	0.029
	2	95.8	4.28	0.057
7	1	97.4	2.62	0.035
	2	97.2	0.736	0.01
8	1	96.0	3.14	0.042
	2	93.5	1.49	0.020
9	2	87.1	1.66	0.022
10	2	92.0	1.52	0.020

TABLE E-13. Daily Effluent Concentrations from Minicolum Tests to Determine Optimum pH for Adsorption of Arsenic(III) onto Activated Alumina

C_o = 1 mg As/L
TDS = 979 mg/L
Cl^- = 7.5 meq/L
SO_4^{2-} = 7.5 meq/L

Day	pH = 4		pH = 5		pH = 6		pH = 7		pH = 8	
	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2
1	0.96	0.96	0.86	0.83	0.91	0.94	0.88	0.86	0.92	0.88
2	1.10	0.92	0.72	0.79	1.00	0.97	0.79	0.76	0.84	0.84
3	1.00	0.79	0.96	1.01	0.97	1.00	0.93	0.88	0.85	0.86
5	0.91	0.91	0.75	0.74	0.86	0.86	1.01	0.96	0.77	0.68
7	0.74	0.70	0.54	0.60	0.95	0.94	0.96	1.00	0.99	0.92
9	0.75	0.76	0.51	0.70	0.96	0.91	1.00	1.01	1.00	0.98
10	0.98	1.00	0.73	0.97	0.89	0.90		1.00	0.86	0.79
12	1.03	0.97	1.00	0.71	0.91	0.89		0.92	0.45	
14	0.96	1.06	0.91	0.76	0.93	0.96		0.97	0.90	0.98